CHAPTER 1

THE KULINKOVICH CYCLOPROPANATION OF CARBOXYLIC ACID DERIVATIVES

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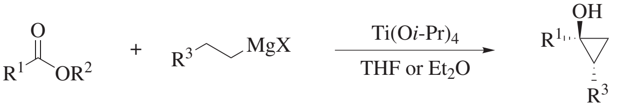
INTRODUCTION

Cyclopropanes are characterized by high ring-strain energy and have been employed as useful building blocks in organic synthesis. The incorporation of a heteroatom donor substituent, such as OH, OR, NR_2, or SR, on the ring imparts enhanced reactivity. Hydroxycyclopropanes (cyclopropanols), in particular, have been thoroughly studied due to their facile ring cleavage. Among several known methods, a new method for the preparation of cyclopropanols involves dialkoxytitanacyclopropane-mediated cyclopropanation (the Kulinkovich cyclopropanation) of esters with a Grignard reagent $R^3CH_2CH_2MgX$ in the presence of titanium isopropoxide (Eq. 1).[1] The striking feature of this method is the facile formation of a three-membered ring from a simple Grignard reagent, which reacts as a 1,2-dicarbanion equivalent through a pivotal dialkoxytitanacyclopropane intermediate (see below).[2] These reactions benefit from the availability of inexpensive reagents, ease of operation, and high selectivity for *cis*-1,2-dialkylcyclopropanols. This cyclopropanation reaction has since been extended to other carboxylic acid derivatives to provide convenient access to several heteroatom-substituted cyclopropanes.[3,4] The utilization of dialkoxytitanacyclopropane (dialkoxytitanium–alkene complex) and dialkoxytitanacyclopropene (dialkoxytitanium–alkyne complex) intermediates has resulted in the development of many useful transformations, which include allylation of carbonyl compounds, carbocyclization reactions of dienes and enynes, allylic alkylation, and carbometallation reactions.[5–9] These reactions are not covered in this chapter.

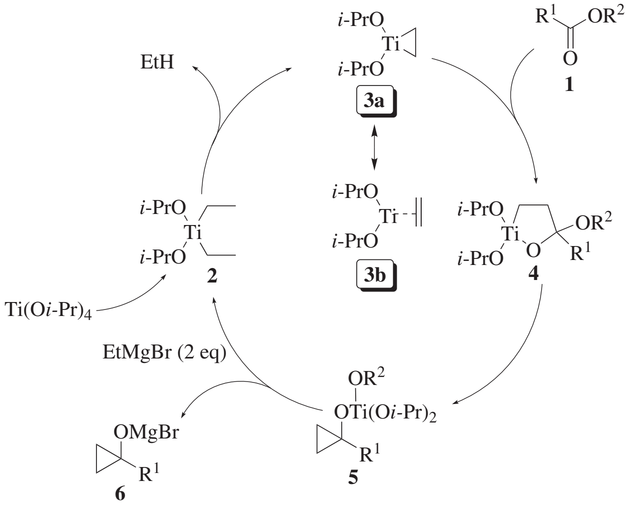


(Eq. 1)

The objective of this review is to provide an updated, comprehensive coverage of the literature on the Kulinkovich cyclopropanation reaction and related processes. Key mechanistic issues are summarized below, and readers are referred to the pertinent literature for additional details and synthetic applications.[3–12b]

MECHANISM AND STEREOCHEMISTRY

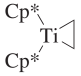
As shown in Scheme 1, the Kulinkovich cyclopropanation of ester **1** is presumed to begin with an initial reaction between Ti(O*i*-Pr)$_4$ and two equivalents of the Grignard reagent, followed by β-hydride elimination from intermediate **2** to produce ethane and the key titanacyclopropane intermediate **3a/3b**. The



Scheme 1. A proposed mechanism for cyclopropanation of an ester with EtMgBr and Ti(O*i*-Pr)$_4$.

latter reacts with ester **1** to afford the cyclopropanolate product **5** through the rearrangement of oxatitanacyclopentane intermediate **4**.[2,13] The catalytic cycle is completed by exchange with the Grignard reagent to deliver **2** and **6**.[2]

The pivotal, proposed intermediate is titanacyclopropane **3a**, which can also be viewed as the ethylene π-complex **3b**. Structural information can be obtained from bis(pentamethylcyclopentadienyl)(ethylene)titanium (**7**), which is prepared by reduction of bis(pentamethylcyclopentadienyl)titanium dichloride with sodium amalgam under an atmosphere of ethylene. The X-ray crystal structure of **7** shows a significant increase in the carbon−carbon bond length to 1.4385(5) Å compared to 1.337(2) Å for free ethylene, as well as considerable displacement of the hydrogen atoms from the planar ethylene geometry.[14] Similar data have also been obtained for the bis(2,6-diphenylphenoxy)(ethylene)titanium complex **8** where the carbon−carbon bond length is 1.425(3) Å.[15] These titanium π-olefin adducts are best characterized as a hybrid of the Ti(II)ethylene and Ti(IV)metallacyclopropane limiting structures.



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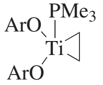
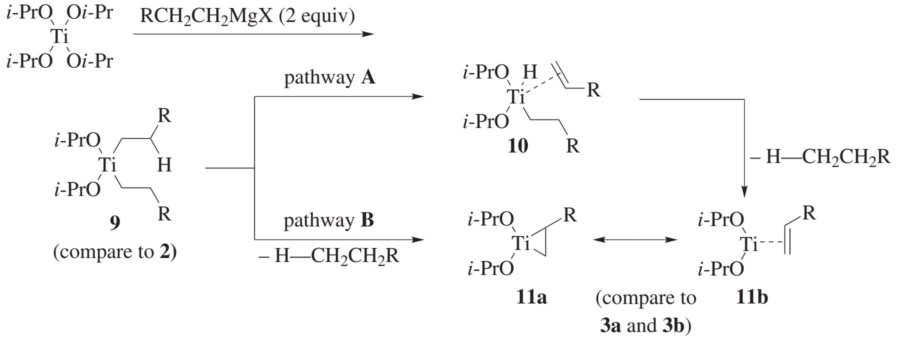


8: Ar = 2,6-$Ph_2C_6H_4$

When homologous Grignard reagents bearing a β-hydrogen atom are employed in place of EtMgBr, the resulting cyclopropanation occurs with high diastereoselectivity for the *cis*-1,2-dialkyl product configuration. Throughout this chapter the *cis*- and *trans*-nomenclature refers to the relationship between two alkyl substituents on a cyclopropane ring instead of following conventional priority rules. Alkyl derivatives of titanium and other transition metals possessing β-hydrogen atoms are readily available, but known to be labile and to undergo decomposition via β-hydride elimination.[16] Generation of a dialkoxytitanacyclopropane species from $Ti(O\textit{i}\text{-}Pr)_4$ by the action of a Grignard reagent is believed to proceed via β-hydride elimination. Deuterium labeling experiments support this and exclude an alternative mechanism involving α-elimination.[17] Closely related precedents can be found in the generation of (ethylene)$ZrCp_2$ (the Dzhemilev reagent) by in situ treatment of Cp_2ZrCl_2 with EtMgBr or Et_2Mg,[18–20] and that of (1-butene)$ZrCp_2$ (the Negishi reagent) by in situ treatment of Cp_2ZrCl_2 with 2 equivalents of *n*-BuLi.[21] The well-known $Cp_2Zr(II)$ and $Cp_2Ti(II)$ chemistry is the subject of numerous reviews.[20,22,23]

Two pathways can be envisioned for the thermal decomposition of dialkyltitanium intermediates **9** (Scheme 2): either a stepwise mechanism involving initial generation of the titanium hydride **10** and subsequent reductive elimination (pathway **A**) or a non-dissociative concerted pathway that affords **11a/11b** and the corresponding alkane (pathway **B**). Disproportionation of **9** to **11** by an epimetalation (coordination-induced reductive elimination) mechanism promoted by an unsaturated functional group (such as a double bond) has also been proposed.[24,25]

The key proposed intermediate **11a/11b** next reacts with a carboxylic ester to provide oxatitanacyclopentane **12**, which undergoes subsequent rearrangement with ring contraction to furnish cyclopropanol **14** (Scheme 3).[13] Although to date details have not been fully elucidated, formation of **12** is believed to arise from insertion of the ester carbonyl group into the less substituted Ti−C bond of **11a/11b**.[26–28] The indicated regiochemistry is also suggested by DFT (density functional theory) calculations.[29] Migration of an alkoxy group is likely to precede the cyclopropane-forming step. The diastereoselective ring closure of titanium homoenolate **13** takes place with retention of configuration at the Ti−C bond with frontside attack on the carbonyl group due to its coordination to titanium.[30,31] The observed preference for *cis*-dialkylated products **14** from unhindered esters could be attributed to the preponderance of **13a** over **13b**, as

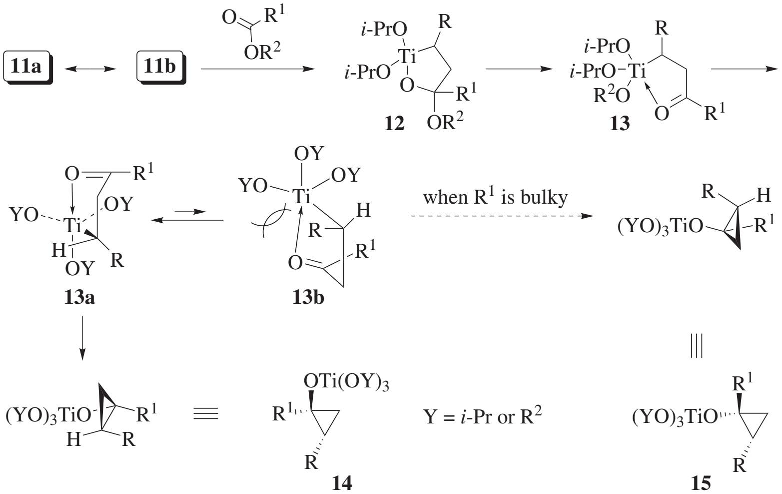


Scheme 2. Two β-elimination pathways.

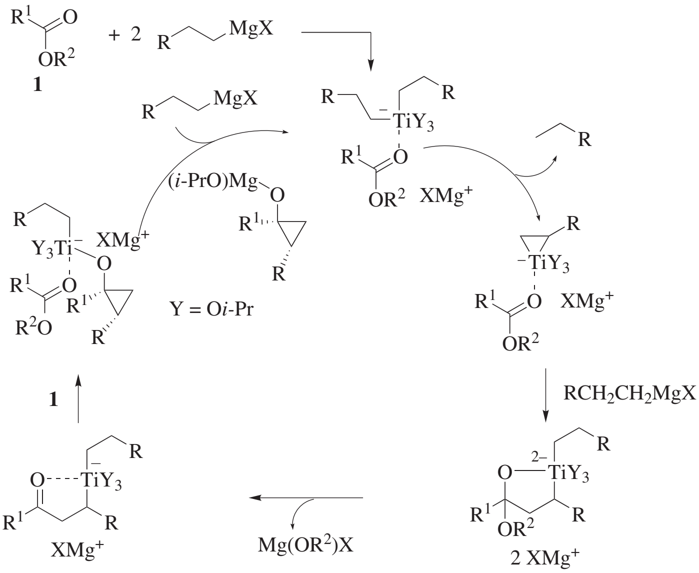
the latter likely suffers from non-bonding interactions between R and Ti(OY)$_3$. A recent theoretical study suggests the importance of a favorable agostic interaction between H and Ti.[29] Although a trigonal bipyramidal geometry is discussed in the computational study (Scheme 3), the octahedral ate complex is likely operating with an alkoxide or alkyl group (from the Grignard reagent) occupying the remaining site (see Scheme 4).

In accord with this model, as R^1 becomes bulky, the intermediate **13a** should become increasingly destabilized by repulsion between the two alkyl substituents R and R^1. Indeed, the Kulinkovich cyclopropanation of α-branched esters, where R^1 is a secondary or tertiary alkyl group, produces a significant amount of the *trans*-dialkylated isomer **15**.[32−34] In view of this outcome it is remarkable that bulky R groups enhance the *cis*-1,2-dialkyl diastereoselectivity.[33]

The precise mechanism of the cyclopropanation reaction is likely to be complex, and Schemes 1 and 3 should be viewed as a useful oversimplification. For example, the mechanisms outlined in these schemes do not account for the unexpected divergence in stoichiometry of Grignard reagents between catalytic and stoichiometric reactions: a catalytic procedure requires approximately 2 equivalents of Grignard reagent. Additional amounts of Grignard reagent are necessary to ensure complete consumption of the ester in a stoichiometric process. A modified mechanism has recently been advanced to rationalize this unusual divergence in stoichiometry and the aforementioned increase of *cis*-1,2-dialkyl diastereoselectivity by bulky R groups (Scheme 4).[34] A stabilizing effect of carboxylic esters on the reduction of Ti(O*i*-Pr)$_4$ with Grignard reagents is also taken into account in this mechanism. Additional data and a detailed discussion of the respective ate-complex mechanism for a stoichiometric cyclopropanation reaction are reported in references 33–35.

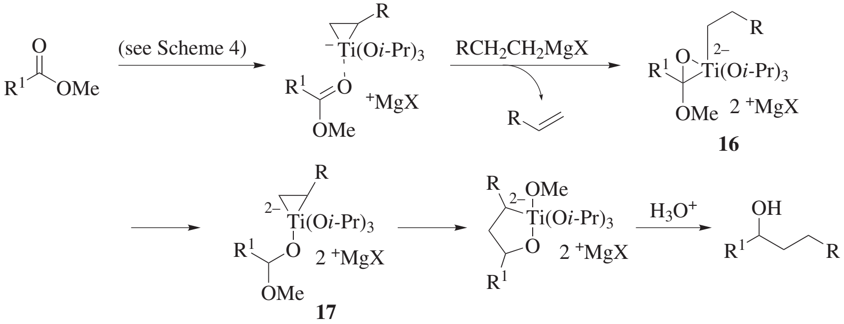


Scheme 3. Generation and diastereoselective ring-contraction of titanium intermediate **12** to afford cyclopropane **14**.



Scheme 4. A mechanism for the catalytic procedure involving an ate-complex.

Small amounts (up to 10–20%) of secondary alcohols are frequently formed in addition to *cis*-1,2-dialkylcyclopropanols. Generation of the former has recently been rationalized by the intermediacy of oxatitanacyclopropane **16** (Scheme 5).[34] A deuterium-labeling experiment suggests a β-hydride abstraction (not shown) in the formation of intermediate **17**.

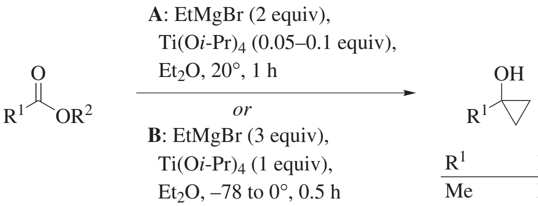


Scheme 5. A proposed mechanism for the formation of secondary alcohol byproducts.

SCOPE AND LIMITATIONS

Cyclopropanation of Esters

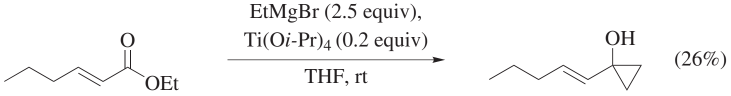
Cyclopropanation of Esters with Grignard Reagents in the Presence of Titanium(IV) Alkoxides. Stoichiometric or catalytic amounts of titanium(IV) alkoxides can be used for the cyclopropanation reaction of carboxylic esters. In a typical reaction, a solution of the Grignard reagent is added slowly to a mixture of an ester and a titanium(IV) alkoxide in diethyl ether, tetrahydrofuran, or other appropriate solvent at room or elevated temperature.[2] When an ethyl Grignard reagent is employed in the presence of 5–20 mol % of the catalyst, a broad range of aliphatic and aromatic carboxylic esters afford the corresponding cyclopropanols in excellent yields. Alternatively, a carboxylic ester may be added to a mixture of the Grignard reagent and $Ti(Oi\text{-}Pr)_4$(1 equivalent) at low temperature, followed by warming the resulting mixture to 0°.[1,13] Both procedures provide 1-alkylcyclopropanols in acceptable yields (Eq. 2).[1,13,36]



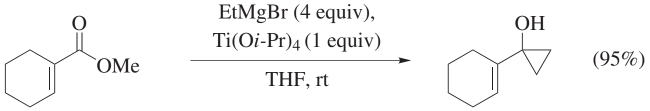
		Yield (%)	
R^1	R^2	**A**[36]	**B**[1]
Me	Et	84	74
n-Pr	Me	87	90
i-Pr	Me	91	88
$n\text{-}C_9H_{19}$	Me	64	98
Ph	Et	64	93

(Eq. 2)

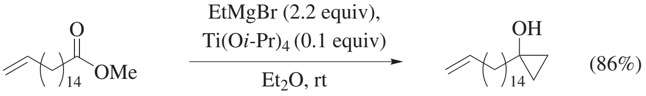
With regard to the scope of the ester substrates, cyclopropanation of acyclic α,β-unsaturated esters is problematic (Eq. 3),[37] but that of their carbocyclic counterparts proceeds in good yields (Eq. 4).[38] The presence of a distal double bond in nonconjugated esters is usually compatible with cyclopropanation (Eq. 5) with the notable exception of the β,γ-unsaturated position.[39] Sequential cyclopropanation and reductive ethylation[40] of β,γ-unsaturated ester **18** gives cyclopropanol **19** in excellent yield when excess amounts of the reagents are used (Eq. 6).[41]



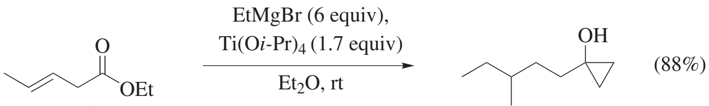
(Eq. 3)



(Eq. 4)



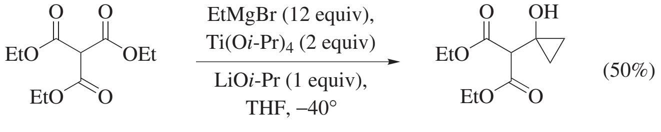
(Eq. 5)



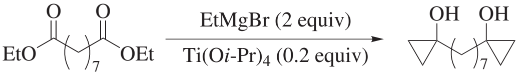
18 **19**

(Eq. 6)

The cyclopropanation reactions of oxalic and malonic esters are unsuccessful. Monocyclopropanation of triethyl methanetricarboxylate proceeds in modest yield by employing lithium isopropoxide as an additive, along with a large excess of ethylmagnesium bromide (Eq. 7).[42] Dicarboxylic esters having more than one methylene spacer undergo clean cyclopropanation to furnish the corresponding bis(cyclopropanols) in THF; ether is a poor solvent due to formation of precipitates (Eq. 8).[43]



(Eq. 7)



Solvent	Yield (%)
ether	0
THF	85

(Eq. 8)

The cyclopropanation reaction of esters is compatible with the presence of many common functional groups. For example, α-trialkylsilyl, α-dialkylamino, and α-alkoxy carboxylic esters are converted into the corresponding cyclopropanols in good yields (Fig. 1).[44–47] The presence of α-halo substituents, however, is incompatible with the Kulinkovich reaction. No complication in the cyclopropanation reaction arises from placement of functional groups (such as halogen, phosphoryl, alkoxy, or acetal) at the β- or more distal positions.[48–50]

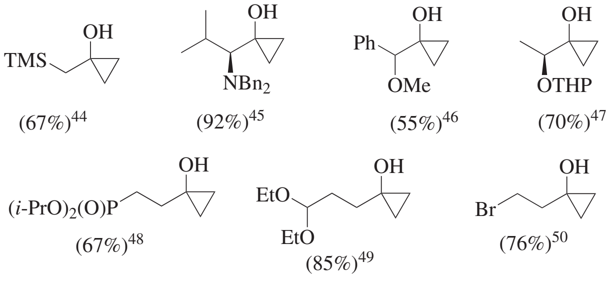
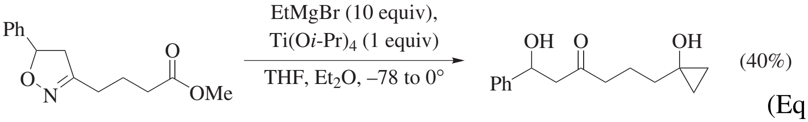
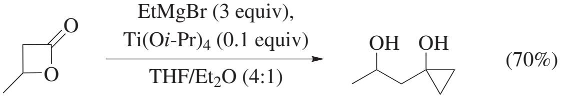


Figure 1. Compatibility of functional groups with the cyclopropanation reaction.

As shown in Eq. 9, an isoxazoline substituent undergoes reduction by a low-valent titanium species concomitant with cyclopropanation to provide a cyclopropanol bearing a β-hydroxy ketone moiety.[51] β-Lactones, as well as higher homologs, are also suitable substrates for the cyclopropanation reaction (Eq. 10).[52]

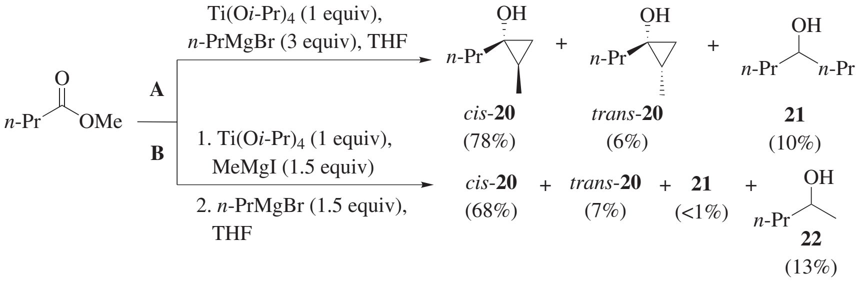


(Eq. 9)

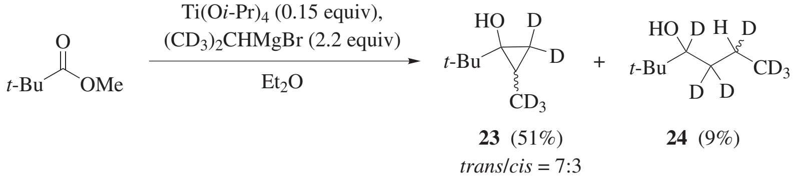


(Eq. 10)

As noted above, homologous Grignard reagents bearing a β-hydrogen atom may be employed in place of ethylmagnesium bromide; typical yields of such cyclopropanations are not as high as those with EtMgBr, but high diastereoselectivity for *cis*-1,2-dialkyl configuration is noteworthy. These *cis*-dialkyl products are easily separable by column chromatography from the corresponding minor *trans* isomers. Under catalytic or stoichiometric reaction conditions (**A**), secondary alcohols such as **21** are usually formed in up to 10–20% yield (Eq. 11).[34] Purification of the reaction mixture can often be complicated due to similar R_f values of *cis*-**20** and **21**. An improved procedure (**B**) that involves addition of 1.5 equivalents of a Grignard reagent to a mixture of 1.5 equivalents of methylmagnesium iodide, one equivalent of Ti(O*i*-Pr)$_4$, and one equivalent of an ester facilitates the purification task because of the considerably lower R_f value of byproducts such as **22**. The reaction of methyl pivaloate with (CD$_3$)$_2$CHMgBr yields cyclopropanol **23** and heptadeuterated alcohol **24** (Eq. 12).[34] Formation of the latter has been attributed to the involvement of oxatitanacyclopropane intermediate **16** in a modified ate complex mechanism (Scheme 5).

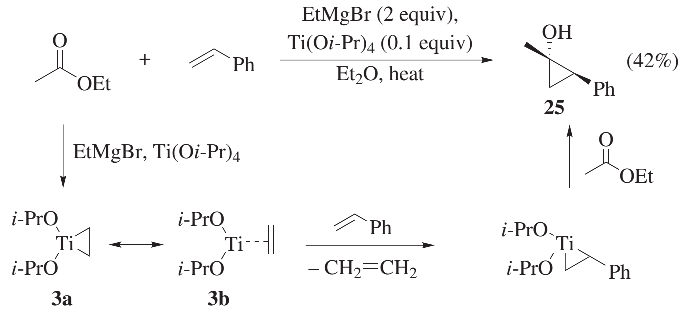


(Eq. 11)



(Eq. 12)

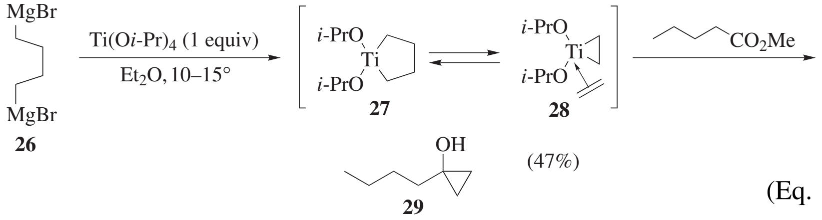
Cyclopropanation of Esters via Olefin Exchange. The scope of the Kulinkovich cyclopropanation of esters has been broadened by exchange of an alkene with the initial dialkoxytitanacyclopropane [Ti(II)–alkene] intermediate. This convenient procedure for generating a new Ti(II)–alkene complex in situ



Scheme 6. Hydroxycyclopropanation of styrene via olefin exchange.

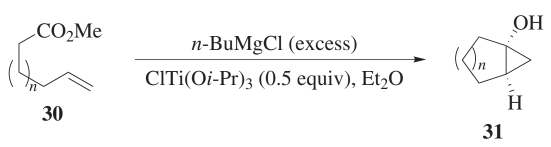
by ligand exchange is reported with styrene in the preparation of cyclopropanol **25** (Scheme 6).[53]

The finding that cyclopropanol **29** is formed by the action of 1,4-bis(bromomagnesio)butane (**26**) on methyl pentanoate in the presence of Ti(O*i*-Pr)$_4$ is in accord with the possible equilibrium between **27** and **28** (Eq. 13).[54]



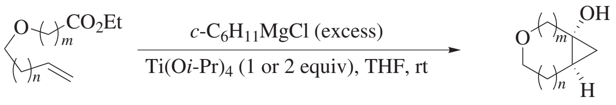
(Eq. 13)

Intramolecular Cyclopropanation of ω-Vinyl-Tethered Esters. An intramolecular variant of the olefin-exchange-mediated cyclopropanation is efficacious and affords bicyclic cyclopropanols in moderate to excellent yields (Eq. 14).[55,56] The intramolecular cyclopropanation of terminal vinyl-tethered esters such as **30** is particularly efficient for formation of five- and six-membered rings (**31**, $n = 1$ and 2), and is also compatible with several common functionalities. However, usually only modest yields are obtained for the annulation of seven-membered rings in the absence of conformational constraints (**31**, $n = 3$). Extension to oxa-ω-alkenoic esters affords seven- and also eight-membered cyclic ethers in higher yields than their all-carbon counterparts (Eq. 15).[57]



n	Yield (%)
1	55
2	62
3	11

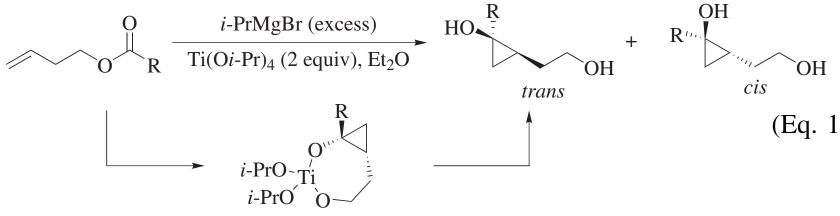
(Eq. 14)



m	n	Yield (%)
1	1	35
2	1	62
2	2	49

(Eq. 15)

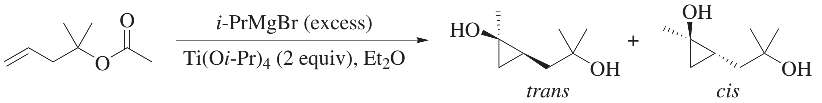
It is noteworthy that use of homoallylic esters leads to *trans*-1,2-dialkylcyclopropanols to complement the intrinsic *cis*-selectivity of the original Kulinkovich reaction (Eq. 16).[55,58] Geometrical constraints of cyclic titanate **32** induced by the pendant alkoxide are believed to account for the observed configuration. Interestingly, the reaction temperature is reported to influence the *trans*/*cis* selectivity (Eqs. 16 and 17).[58] This method is useful for preparing cyclopropanols containing alkenyl or phenyl groups at C1,[37] whereas the original Kulinkovich procedure with Grignard reagents other than ethylmagnesium bromide is unsatisfactory for benzoates and many α,β-unsaturated esters.



32

(Eq. 16)

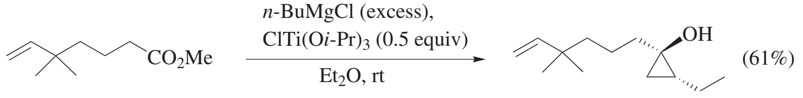
R	Temp (°)	Yield (%)	*trans*/*cis*
i-Pr	–40 to 0	88	88:12
CH=CHMe	–40 to 20	73	100:0
CH=CHMe	–40 to 0	78	93:7
Ph	–40 to 0	85	97:3
Ph	rt	78	88:12



Temp (°)	Yield (%)	*trans*/*cis*
–40 to 0	28	47:53
–40 to 20	78	91:9

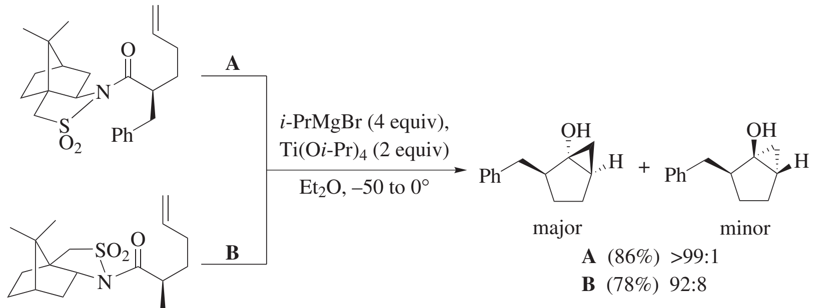
(Eq. 17)

In addition to the above-mentioned modest yields for formation of seven-membered rings, intramolecular cyclopropanation is limited primarily to monosubstituted olefins. Neither di- nor trisubstituted olefin-tethered esters usually undergo cyclization. Instead, the intermolecular products, i.e., the original Kulinkovich reaction products derived from the Grignard reagent, are obtained. Similarly, bulky substituents at the allylic position of terminal vinyl groups preclude the cyclopropanation reaction (Eq. 18).[55] These results clearly point to the importance of steric accessibility of π-electrons toward the titanium atom for the formation of the key titanacyclopropane intermediate.



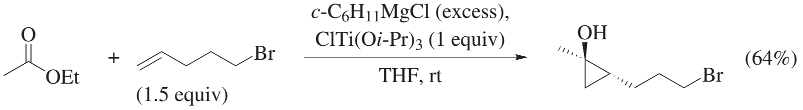
(Eq. 18)

Another drawback is the lack of diastereocontrol exerted by a resident stereocenter on the *cis*-dialkylated cyclopropanol products. However, a diastereoselective cyclization is achieved by employing the *N*-acylcamphorsultam chiral auxiliary (Eq. 19).[59]

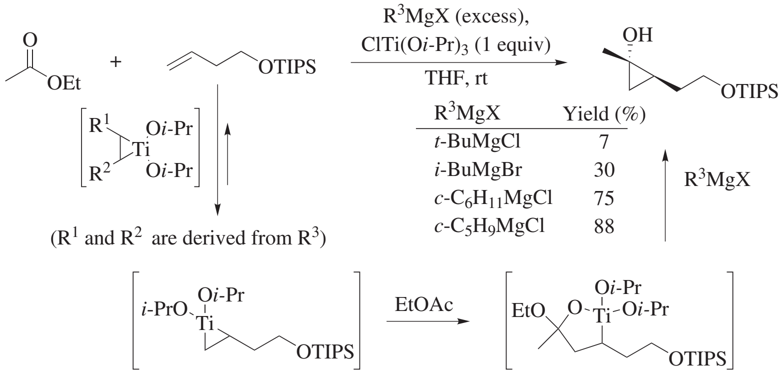


(Eq. 19)

Intermolecular Cyclopropanation of Esters with Alkenes. Despite the successful reductive coupling of esters with styrene (Scheme 6),[53] direct adaptation of the olefin exchange to other terminal olefins such as 1-heptene is unsatisfactory when employing ethyl or butyl Grignard reagents. An effective solution utilizes cyclohexyl or cyclopentyl Grignard reagents, which help shift the key equilibrium in the desired direction from the less stable, disubstituted titanacyclopropane intermediates derived from these secondary Grignard reagents to the more stable, monosubstituted counterparts resulting from olefin exchange (Scheme 7).[60,61] Typically, these cyclopropanation reactions are performed at room temperature or 0°, as poor yields are obtained at temperatures below $-10°$ to about $-20°$ (Eqs. 20 and 21).[60] Although ethers such as diethyl ether, THF, or dioxane are most frequently used as solvents, non-ethereal solvents such as benzene or toluene may also be employed.

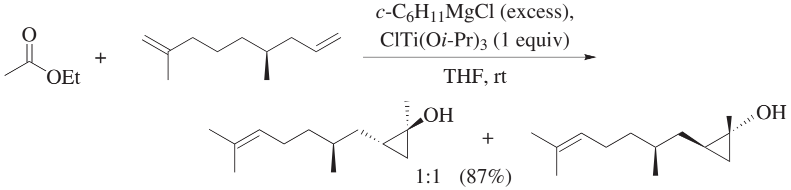


(Eq. 20)



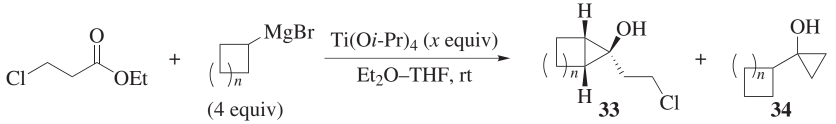
R^{3}MgX	Yield (%)
t-BuMgCl	7
i-BuMgBr	30
c-C$_6$H$_{11}$MgCl	75
c-C$_5$H$_9$MgCl	88

Scheme 7. Intermolecular cyclopropanation of esters by ligand exchange.



(Eq. 21)

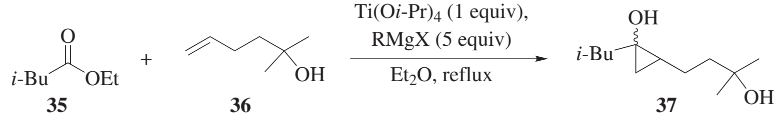
Additionally, this variant of utilizing inexpensive cyclohexyl or cyclopentyl Grignard reagents as a sacrificial source for a Ti(II)–cycloalkene complex is compatible with many useful functional groups. Lactones undergo the titanium-mediated cyclopropanation with terminal olefins; recent examples include not only γ- and δ-lactones, but also β-lactones.[47] Non-conjugated polyenes are amenable to hydroxycyclopropanation with selective reaction at the monosubstituted double bonds. The olefin-exchange-mediated hydroxycyclopropanation of norbornene is a notable exception to the rule that disubstituted alkenes do not usually react, presumably because of relief of the strain of its double bond.[60] It should be noted, however, that the original Kulinkovich reaction procedure involving direct addition of cyclopentyl or cyclohexyl Grignard reagents[62] gives 1,2,3-trisubstituted cyclopropanols **33** in poor or moderate yields, sometimes along with a side-product **34** (Eq. 22).[63]



		Yield (%)	
n	*x*	**33**	**34**
1	0.2	46	0
2	1	63 *exo*/*endo* 63:37	0
3	1	17	46
4	0.2	56	2

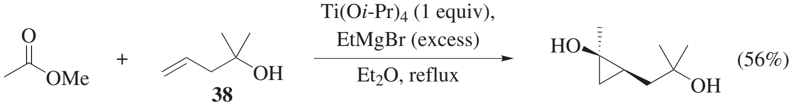
(Eq. 22)

When a hydroxy group or a heteroatom is present in the olefin, Grignard reagents other than *c*-C_5H_9MgCl and *c*-$C_6H_{11}MgCl$ can be used. For example, use of EtMgBr affords the best yield for coupling of ester **35** and alcohol **36** for the preparation of **37** (Eq. 23)[64,65] and is also effective for the corresponding hydroxycyclopropanation of tertiary alcohol **38** (Eq. 24).[64] With acetal **39**, *n*-BuMgCl and EtMgBr may be employed for the cyclopropanation (Eq. 25).[66,67]

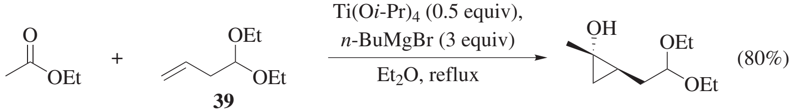


RMgX	Yield (%)	
EtMgBr	72	(85 with 1.2 equiv of **35**)
i-PrMgBr	63	
n-BuMgCl	62	
c-$C_6H_{11}MgCl$	33	

(Eq. 23)



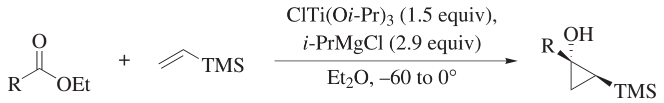
(Eq. 24)



(Eq. 25)

One notable limitation in the scope is that applications of this ligand-exchange variant to aromatic esters such as benzoates have been unsuccessful. By contrast, treatment of the Negishi zirconocene, which is generated in situ from zirconocene dichloride and two equivalents of *n*-butylmagnesium bromide, with methyl benzoate gives the respective cyclopropanol in 91% yield (9:1 diastereoselectivity).[68] It is unclear, however, whether this method is amenable to an olefin exchange modification.

Vinylsilanes are useful for cyclopropanation of both aromatic and aliphatic esters. Thus, treatment of trimethyl(vinyl)silane and an ester with *i*-PrMgCl in the presence of Ti(O*i*-Pr)$_4$ affords cyclopropanols in good yields (Eq. 26).[69] One striking example is the exclusive intermolecular cyclopropanation of methyl 6-heptenoate in preference to the intramolecular reaction.

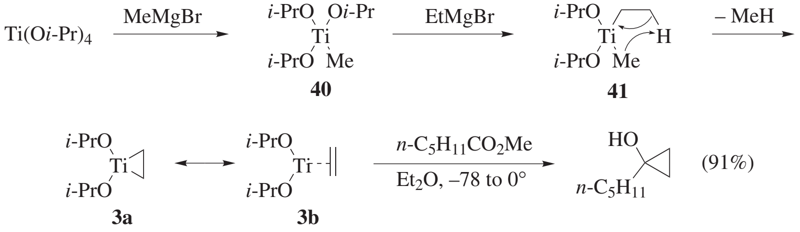


R	Yield (%)	dr
n-Pr	80	87:13
CH_2=CH(CH_2)$_4$	62	88:12
Ph	88	93:7
PhCH_2CH_2	76	81:19

(Eq. 26)

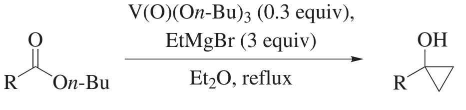
A decrease in *cis/trans* diastereoselectivity is observed for esters sterically hindered at the α-carbon. Additionally, substituents at the allylic position of terminal olefins impede these reactions. Under typical reaction conditions, allylic alcohols, ethers, and halides undergo facile elimination to generate allyltitanium derivatives, which are used in a wide variety of synthetically useful transformations. These reactions, which are not covered here, are the subject of a number of reviews.[5–9]

Variation of the Titanium Alkoxide. Titanium(IV) isopropoxide and chlorotriisopropoxytitanium(IV) can be used interchangeably, and Grignard reagents with groups larger than ethyl are reported to give better yields with the latter.[70] Use of methyltriisopropoxytitanium (**40**) is advantageous,[62,71] because one less equivalent of the homologous Grignard reagent is required than under the original Kulinkovich reaction conditions (i.e., ≥2 equivalents) due to generation of methane by β-elimination from intermediate **41** (Eq. 27).[71] Several titanium alkoxides and phenoxides have been evaluated under both the original Kulinkovich conditions and the olefin-exchange modification;[72] the original procedure is insensitive to the nature of the titanium alkoxide, including $Ti[OCH(CF_3)_2]_4$, and aryloxides. On the other hand, the olefin-exchange-mediated cyclopropanation is dependent upon the nature of the titanium reagents. Titanium alkoxides are more effective than titanium phenoxides. Additionally, poor yields are obtained when an electron-withdrawing substituent is present in the alkoxy group (e.g., $Ti[OCH(CF_3)_2]_4$) because of the lability of the presumed Ti(II)−alkene complex.[72] Overall, Ti(O*i*-Pr)$_4$, ClTi(O*i*-Pr)$_3$, or MeTi(O*i*-Pr)$_3$ (**40**) appears to be the reagent of choice, with the latter two compounds affording slightly improved yields.



(Eq. 27)

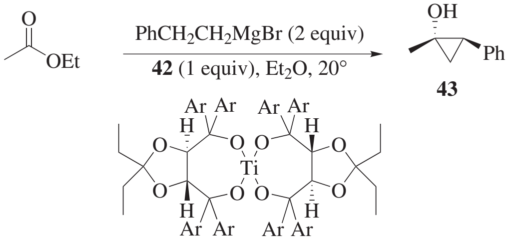
Tributyl vanadate(V) has also been employed in the cyclopropanation of esters (Eq. 28).[73] Additional studies on cyclopropanation with vanadium alkoxides could yield useful information about the reactivity of the vanadacyclopropane species.



R	Yield (%)
n-C$_5$H$_{11}$	83
c-C$_6$H$_{11}$	51
trans-2-hexenyl	48
n-C$_7$H$_{15}$	78

(Eq. 28)

Enantioselective Cyclopropanation of Esters. Asymmetric synthesis of (1*S*,2*R*)-2-phenyl-1-methylcyclopropanol (**43**) is achieved in an enantiomeric excess of up to 78% by the action of TADDOLate **42** (Eq. 29).[70] Additional studies with chiral titanium(IV) alkoxides could serve not only to optimize the enantioselectivity, but also to delineate the scope and limitations of this reaction.



(Eq. 29)

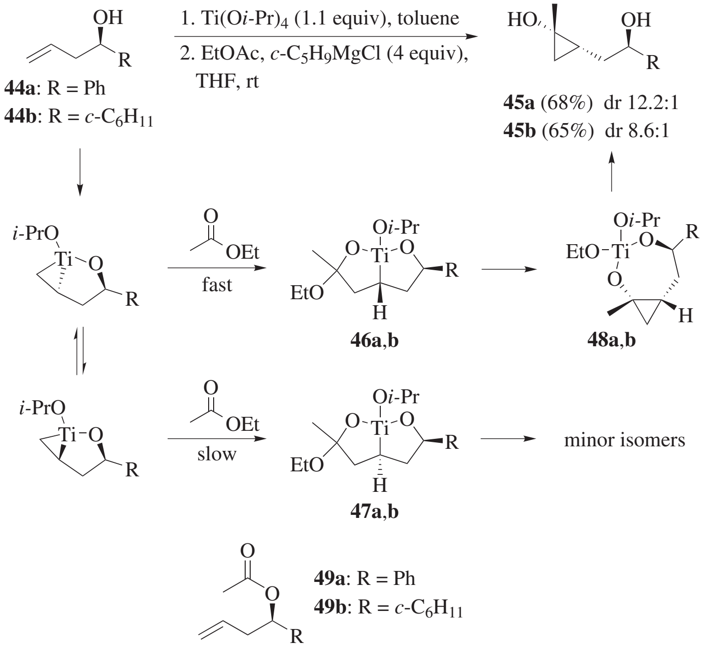
42: Ar = 3,5-bis(trifluoromethyl)phenyl

Diastereoselective Hydroxycyclopropanation with Homoallylic Alcohols. An alternative approach to enantioselective synthesis of 1,2-dialkylcyclopropanols entails the hydroxycyclopropanation of secondary homoallylic alcohols involving in situ generation of a mixed titanate and takes advantage of the ready availability of enantiomerically pure starting alcohols. *trans*-1,2-Dialkylcyclopropanols are prepared in moderate to good levels of diastereoselectivity by the intermediacy of the bicyclic titanacyclopropanes derived from homoallylic alcohols, for example, alcohols **44a** and **44b** (Scheme 8).[74] Preferential formation of intermediates **46a** and **46b** over **47a** and **47b** accounts for the observed 1,3-diastereoselectivity. The *trans*-1,2-dialkyl selectivity is attributed to geometrical constraints imposed by the seven-membered cyclic titanate intermediates **48a** and **48b**, as is the case in Eq. 16. It is interesting to note that the intramolecular cyclopropanation of acetates **49a** and **49b** gives 1:1 mixtures of cyclopropanes **45a** and **45b** and the other *trans*-dialkyl diastereomers in 73% and 61% yields, respectively, with no 1,3-diastereocontrol.[74]

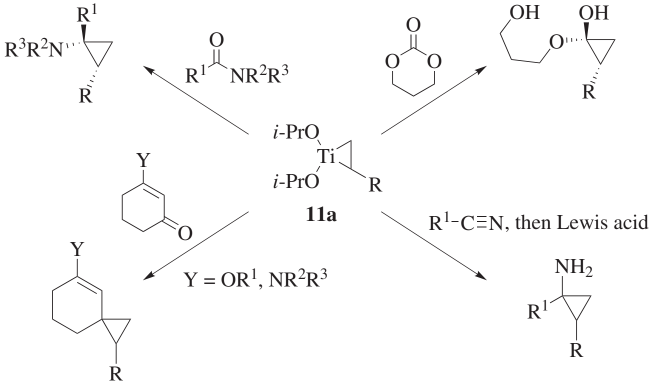
Cyclopropanation of Other Carboxylic Acid Derivatives and Related Carbonyl Compounds

The Kulinkovich cyclopropanation of esters has been extended to other carboxylic acid derivatives to provide convenient access to the corresponding heteroatom-substituted cyclopropanes (Scheme 9). As described for the cyclopropanation of esters, the requisite titanacyclopropane intermediate **11** is generated by direct treatment of Grignard reagents with titanium(IV) alkoxides or by olefin exchange. Selected cyclopropanation reactions are summarized in Scheme 9. A complete survey is found in the tables, and each substrate class will be covered in the following sections.

Cyclopropanation of Amides. Treatment of tertiary carboxamides with Grignard reagents in the presence of $Ti(O\textit{i}\text{-}Pr)_4$, $ClTi(O\textit{i}\text{-}Pr)_3$, or $MeTi(O\textit{i}\text{-}Pr)_3$ affords cyclopropylamines in good yields (Scheme 10).[62,75,76] The diastereoselectivity varies and is typically modest, especially compared to that

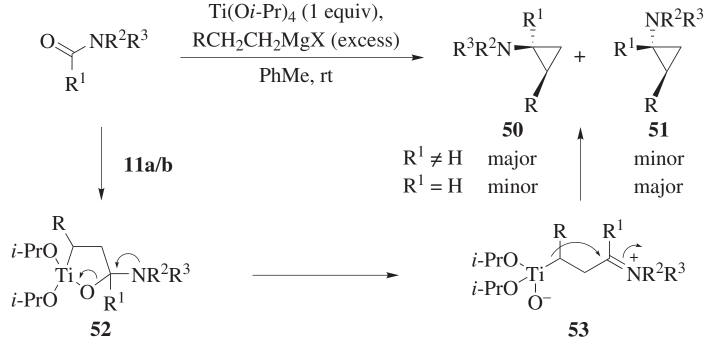


Scheme 8. *trans*-Dialkyl-selective cyclopropanation with secondary homoallylic alcohols.



Scheme 9. Preparation of heteroatom-substituted cyclopropanes from carboxylic acid derivatives.

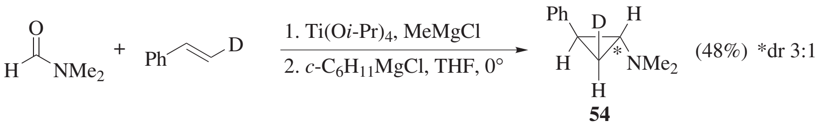
of the cyclopropanation of esters, and usually favors the *trans*-1,2-dialkyl isomers (e.g., **50**).[77] In the case of formamides ($R^1 = H$), the *cis* isomers **51** are the major products. After initial formation of intermediate **52** by coupling of **11a/b** and an amide, this reaction is proposed to proceed via iminium ion intermediate **53**. The final ring closure takes place with inversion of configuration at the titanium–carbon bond via the W-shaped geometry shown (see below).[30,78] Steric



Scheme 10. Cyclopropanation of amides by adaptation of the Kulinkovich reaction.

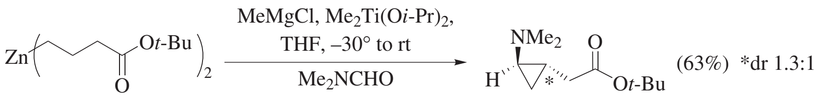
effects appear to be the dominant factor. When $R^1 \neq H$, the *trans*-1,2-dialkyl isomers **50** are favored to avoid nonbonding interactions between R^1 and R, which are more severe than those between R and the iminium ion moiety. With formamides, where the iminium ion group is bulkier than $R^1 = H$, the opposite stereochemical preference (formation of isomer **51**) is observed, albeit with poor to modest diastereoselectivity.

Inversion of configuration at the carbon atom bound to the titanium in the final ring-closing step of intermediate **53** has recently been confirmed by employing *trans*-β-deuterostyrene in the synthesis of deuterocyclopropane **54** (Eq. 30).[30,31] This stereochemical outcome contrasts with the retention of configuration observed at the Ti−bonded carbon from frontside attack on the carbonyl group in the Kulinkovich cyclopropanation of esters.



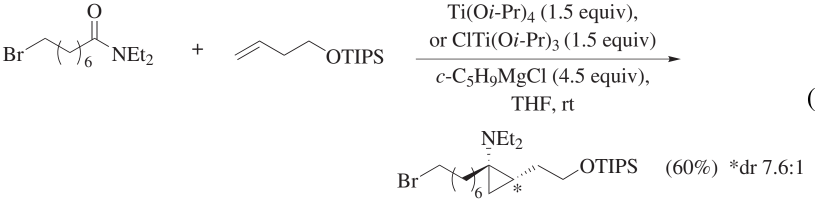
(Eq. 30)

The relative reactivity of amides and esters towards **11a/b** has been assessed by competition experiments.[79] Given similar conditions, esters are more reactive than amides. However, the intrinsic reactivity of acyl derivatives is subject to reversal by steric effects. For example, *tert*-butyl esters are less reactive than unhindered tertiary amides, and the former can be introduced into aminocyclopropanes by employing organozinc reagents in place of Grignard reagents (Eq. 31).[80]

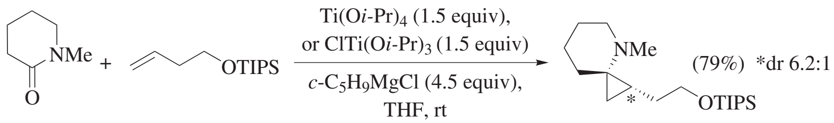


(Eq. 31)

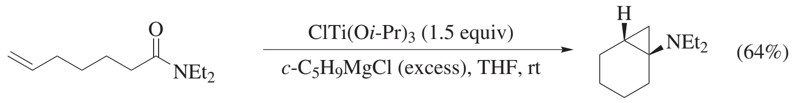
The ligand exchange modification has been successfully utilized for inter- and intramolecular cyclopropanation of amides (Eqs. 32–35).[77] The reported yields for a range of tertiary amides (or lactams) and terminal olefins vary from moderate to high. Because of the substantially lower reactivity of amides than that of esters toward competing nucleophilic attack by Grignard or the corresponding titanium reagents, cyclization of ω-vinyl amides is often more efficient than that of the ester counterparts, and this trend (higher yields from **55a** to **55c**) is clearly seen in the challenging formation of seven-membered ring **56** (Eq. 36).[81]



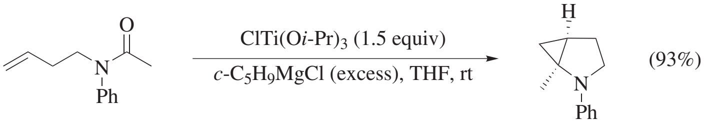
(Eq. 32)



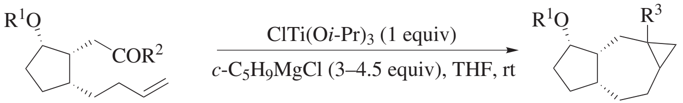
(Eq. 33)



(Eq. 34)



(Eq. 35)

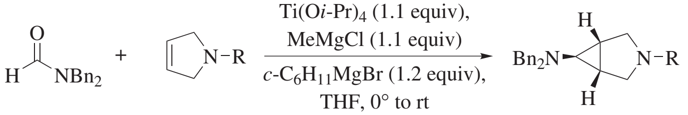


56

(Eq. 36)

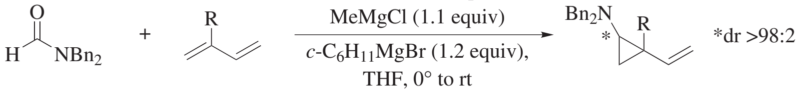
Ester	R^1	R^2	R^3	Yield (%)
55a:	Me	OMe	OH	40
55b:	TIPS	NEt_2	NEt_2	52
55c:	TIPS	NBn_2	NBn_2	78

With regard to scope, α,β-unsaturated amides fail to give the corresponding cyclopropylamines, but instead undergo reduction.[77] Not only terminal olefins, but also disubstituted olefins and 1,3-dienes are amenable to coupling with amides for the preparation of aminocyclopropanes (Eqs. 37 and 38).[82] Cyclopentene and pyrrolines are particularly well suited for aminocyclopropanation.[82,83] Cyclic 1,3-dienes, acyclic counterparts with one terminal vinyl group, and even trienes have also been employed. In contrast, hydroxycyclopropanation of 1,3-dienes with esters has been problematic, where bifurcation of closely related intermediates to an alternate pathway becomes dominant.[84] An intramolecular cyclopropanation of amide **57** for the preparation of **58** provides further unambiguous evidence for the above-mentioned inversion of configuration at a Ti–bound carbon in the ring-closing step, although the yield is modest (Eq. 39).[78]



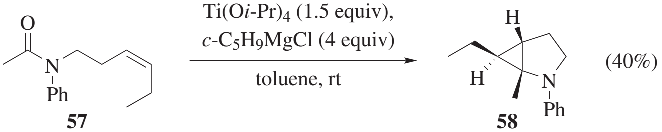
R	Yield (%)
Boc	90
Bn	87

(Eq. 37)



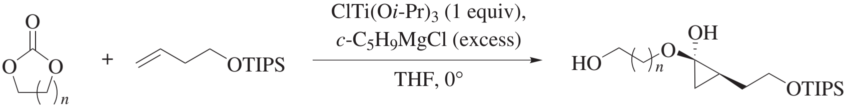
R	Yield (%)
Me	59
$(CH_2)_2CH{=}CMe_2$	51

(Eq. 38)



57 **58** (Eq. 39)

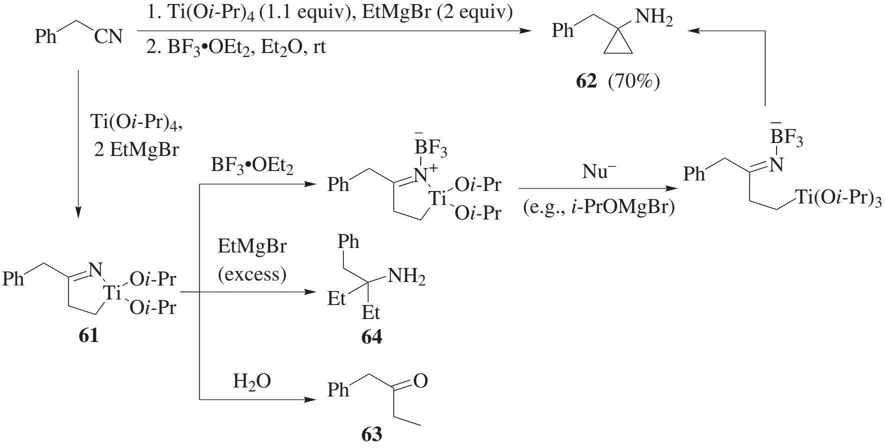
Cyclopropanation of Carbonates. A new route to the synthetically useful cyclopropanone hemiacetals is available by coupling of terminal olefins with ethylene or propylene carbonate (Eq. 40).[85,86] Although yields are only moderate, a broad range of functional groups can be conveniently incorporated into otherwise inaccessible target compounds. Interestingly, use of propylene 1,3-carbonate affords product **60** as a single diastereomer in 53% yield, whereas ethylene 1,2-carbonate gives product **59** with a dr of 2:1. However, use of acyclic carbonates affords poor (≤30%) yields. The corresponding intramolecular reactions of dialkoxytitanacyclopropanes with carbonates of homoallylic, homopropargylic, and homoallenyl alcohols do not result in formation of a three-membered ring, but instead offer an interesting route to functionalized esters or lactones.[85,87,88] Dialkoxytitanacyclopropanes also react with carbon dioxide to afford carboxylic acids.[89,90]



	n	Yield (%)	dr
59:	1	47	2:1
60:	2	53	1:0

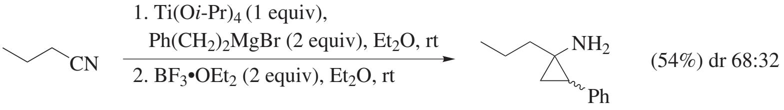
(Eq. 40)

Cyclopropanation of Nitriles. Primary cyclopropylamines **62** are readily available by adaptation of the Kulinkovich reaction to nitriles and subsequent addition of a Lewis acid such as $BF_3{\cdot}OEt_2$ or $TiCl_4$ to induce the ring contraction of intermediate **61** (Scheme 11).[91] In the absence of a Lewis acid, ketone **63** is the main product, along with a small amount of the cyclopropylamine **62**. An excess (more than 2 equivalents) of the Grignard reagent is detrimental to three-membered ring formation, as it affords the double addition product **64** in 67% yield. α-Alkoxy-, α-dialkylamino-, and β-carboalkoxy nitriles do not require addition of a Lewis acid for successful cyclopropanation, as the chelate formation between an α- or β-heteroatom and the imino group by a titanium or magnesium metal induces the ring contraction.[92,93] Lithium iodide is used in the preparation of 1-aryl-substituted cyclopropylamines from aromatic nitriles, MeTi(O*i*-Pr)$_3$, and diethylzinc.[76,94]

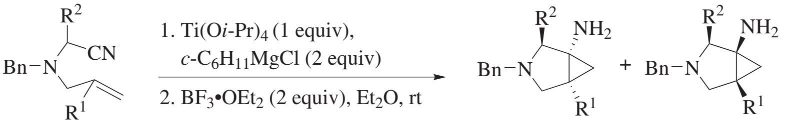


Scheme 11. Titanium-mediated cyclopropanation of nitriles.

Use of Grignard homologs other than ethylmagnesium bromide and also the intramolecular aminocyclopropanation of unsaturated nitriles by the action of cyclohexylmagnesium chloride have been reported (Eqs. 41–43).[91,95] No *cis*/*trans* diastereoselectivity is observed. Diastereocontrol by a resident stereocenter is low in an intramolecular process,[95] as is the case in the cyclopropanation reactions of esters and amides. Interestingly, the intramolecular reactions for formation of five-membered bicyclic compounds proceed without a Lewis acid additive in comparable (67% vs 59%) yields.[95] Disubstituted olefins also undergo intramolecular aminocyclopropanation. Competition experiments show that nitriles are more reactive than esters and amides, and the greater reactivity of nitriles allows convenient preparation of functionalized aminocyclopropanes containing esters and amides.[96,97] An olefin-exchange-mediated intermolecular cyclopropanation of nitriles is difficult to achieve.[95,98] However, intermolecular cyclopropanation between nitriles and homoallylic alcohols is reduced to practice by taking advantage of preassociation of the homoallylic alkoxide and a titanacyclopropane complex (Eq. 44).[99]

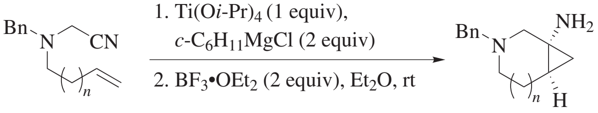


(Eq. 41)



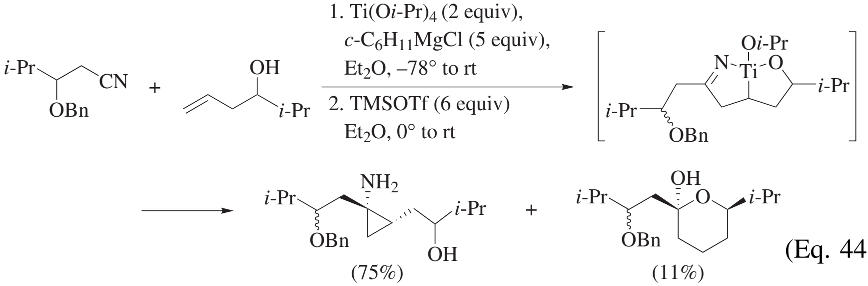
(Eq. 42)

R^1	R^2	Yield (%)	dr
H	Et	67	72:28
Me	H	69	—



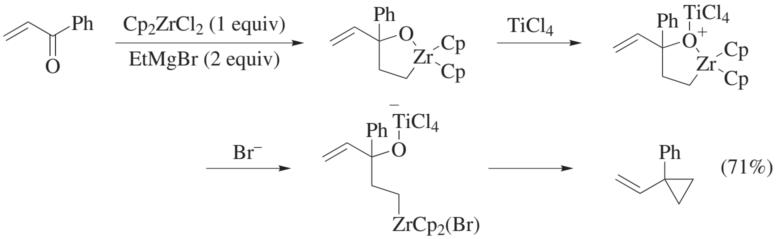
n	Yield (%)	
		w/o BF$_3$•OEt$_2$
1	60	11
2	27	—

(Eq. 43)



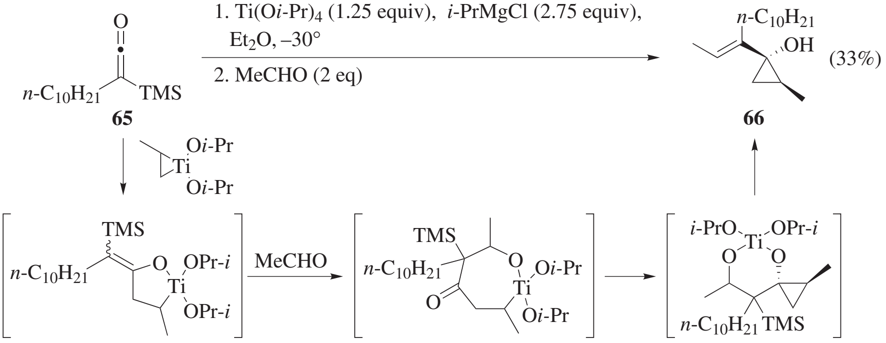
(Eq. 44)

The use of a Lewis acid to promote the ring contraction of a metallacycle has precedent in a deoxygenative cyclopropanation reaction of unsaturated and saturated ketones and aldehydes (Eq. 45).[100] This approach has been extended to the preparation of cyclopropanes from allylic ethers by initial hydrozirconation and subsequent addition of TiCl$_4$.[101] In both reactions, the key cyclopropanation proceeds with inversion of configuration at the carbon bound to zirconium in a W-shaped transition state.[30]



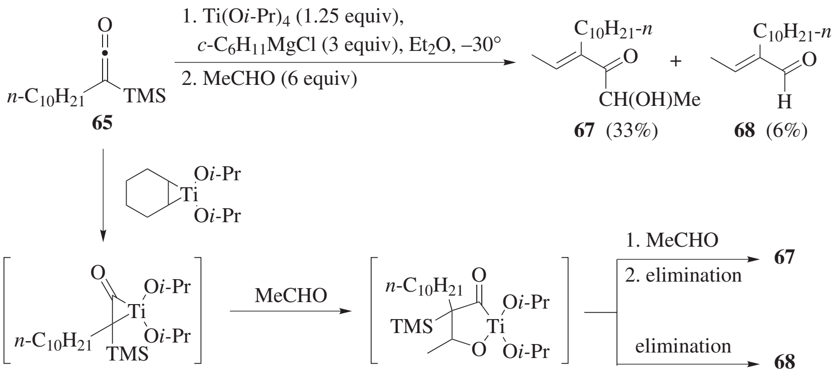
(Eq. 45)

Cyclopropanation of Silyl Ketenes. Silyl ketenes can also undergo cyclopropanation under Kulinkovich reaction conditions. Treatment of silyl ketene **65** with Ti(O*i*-Pr)$_4$ and isopropylmagnesium chloride, followed by addition of acetaldehyde, gives alkenylcyclopropanol **66** as a single isomer (Scheme 12).[102] In contrast, use of cyclohexylmagnesium chloride affords enone **67** and the corresponding aldehyde **68** by a Peterson elimination of the presumed intermediate (Scheme 13).[102]

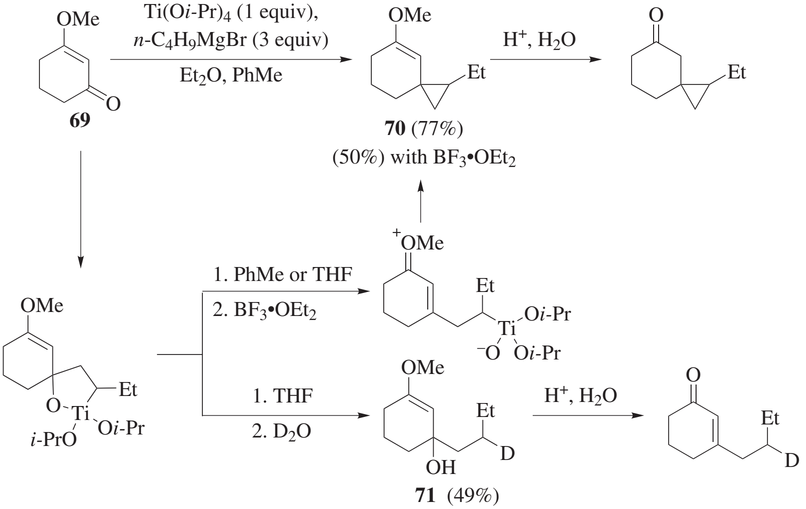


Scheme 12. Titanium-mediated cyclopropanation of a silylketene.

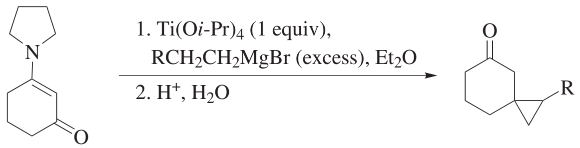
Cyclopropanation of Vinylogous Esters and Amides. Vinylogous esters and amides are converted into the cyclopropanes by the action of titanacyclopropanes (Scheme 14[98] and Eq. 46[103]). Remarkable solvent effects are noted; cyclopropane **70** is formed exclusively in 77% yield from substrate **69** in toluene, whereas an alkylation product **71** is obtained in 49% yield in THF. Both are isolated as the corresponding ketones after mild acidic hydrolysis of the enol ether functionality. The solvent effects can be overridden by addition of a Lewis acid such as BF$_3$•OEt$_2$.



Scheme 13. Titanium-mediated reaction of a silylketene with cyclohexylmagnesium chloride.



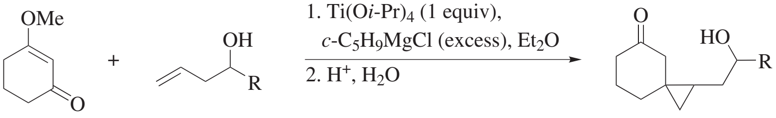
Scheme 14. Cyclopropanation of a vinylogous ester.



R	Yield (%)
H	57
Et	83
Ph	83

(Eq. 46)

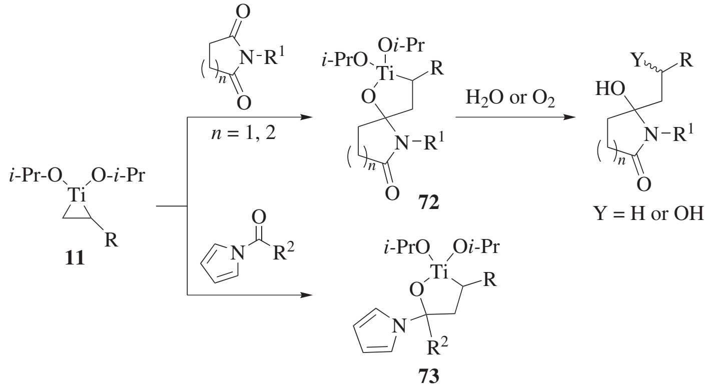
Implementation of the typical olefin exchange procedure to coupling of vinylogous esters and terminal olefins does not produce the corresponding cyclopropanes, and only poor yields (36%) are obtained from vinylogous amides. A satisfactory solution is the use of homoallylic alcohols (Eq. 47).[98] A number of synthetic applications take advantage of the unique directing effects of the mixed titanates derived from homoallylic and homopropargyl alcohols.[64,65,104,105]



R	Yield (%)
H	45
Bn	52

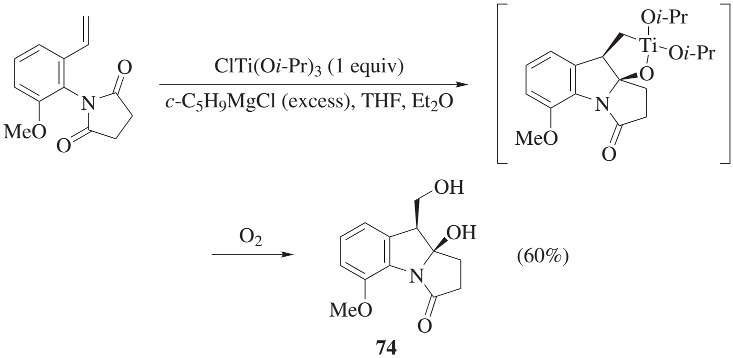
(Eq. 47)

Dialkoxytitanacyclopropane-Mediated Reactions of Imides and *N*-Acylpyrroles. In contrast to the titanium-mediated cyclopropanation of esters, amides, carbonates, and nitriles, coupling of a dialkoxytitanacyclopropane intermediate with carboxylic acid derivatives containing a non-basic nitrogen such as imides[26] and *N*-acylpyrroles[27] does not readily afford heteroatom-substituted cyclopropanes. The resulting oxatitanacyclopentanes **72** and **73** are stable and are typically subjected to protonolysis or oxidation without isolation (Scheme 15).[26,27] As noted earlier, the less substituted Ti–C bond of **11** adds to the carbonyl group of both imides and *N*-acylpyrroles. By analogy, the same regiochemistry as in the Kulinkovich cyclopropanation of esters is believed to be involved.



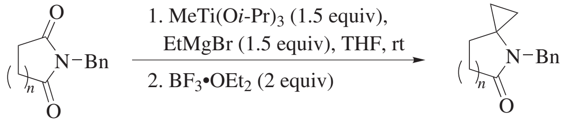
Scheme 15. Coupling of titanacyclopropane **11** with imides and *N*-acylpyrroles.

An intramolecular variant using ω-vinyl imides provides a convenient method for the stereocontrolled syntheses of several alkaloids.[26,106,107] The resulting *N*-acyl hemiaminal products **74** (Eq. 48)[26] are well suited for further transformations such as reduction and C–C bond formation. This titanium-mediated cyclization of ω-vinyl imides complements the well-known *N*-acyliminium ion chemistry.[108–111]



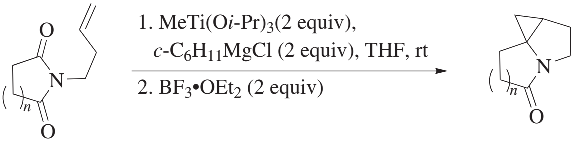
(Eq. 48)

Upon addition of a Lewis acid, oxatitanacyclopentane intermediates such as **72** undergo ring closure to give aminocyclopropanes **75–78** (Eqs. 49 and 50).[112]



	n	Yield (%)
75:	1	79
76:	2	67

(Eq. 49)



	n	Yield (%)
77:	1	65
78:	2	62

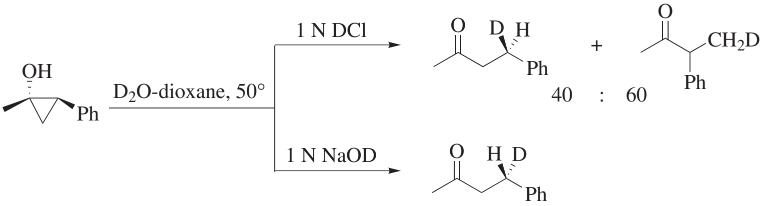
(Eq. 50)

APPLICATIONS TO SYNTHESIS

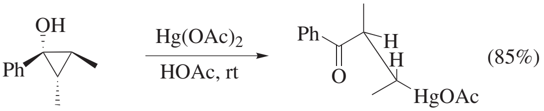
Ring opening or expansion of cyclopropanes is accompanied by release of ring strain, which has been exploited in C−C bond formation. Ring opening is induced by the action of electrophiles such as proton donors, halogenating agents, and transition- or non-transition-metal salts.[113−118] Extensive studies have been directed to examine the site- and stereoselectivity of these electrophilic ring-opening reactions of cyclopropanes. Both modes of "corner" and "edge" attack are known: electrophiles, ring substituents, and geometrical factors affect the mechanism.[118] Synthetically useful ring-cleavage reactions typically involve cyclopropylcarbinyl cations, halogenated cyclopropanes, and cyclopropanes containing activating groups. Incorporation of electron-donating or -withdrawing groups activates cyclopropanes toward ring opening by electrophiles or nucleophiles, respectively. Juxtaposition of both electron-donating and -withdrawing groups in geminal and vicinal positions provides another interesting approach to controlling reactivity. In addition to facile ring scission, these functional groups are also useful for subsequent elaboration.[119−123] The chemistry of donor-acceptor, sila-, and halogenated cyclopropanes is not reviewed herein and the readers are referred to reviews.[119−125] This concise summary focuses on selected examples of synthetic uses of cyclopropanes substituted with hydroxy, siloxy, and amino groups. Detailed discussions can be found in recent reviews.[10,125−135]

Applications of Cyclopropanols and Derivatives

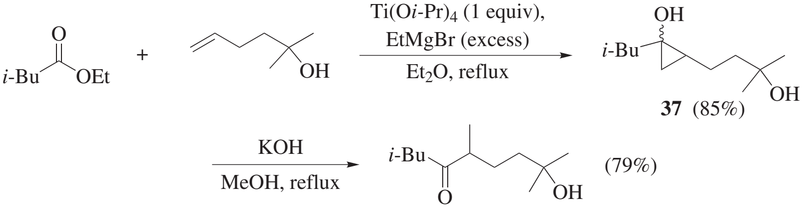
The enhanced reactivity of cyclopropanols has long been recognized.[125] Ring opening of a cyclopropanol can be induced by the action of base and a one-electron oxidant, as well as by electrophiles, which renders it a homoenol equivalent. Electrophilic opening reactions of cyclopropanols are sensitive to steric hindrance and electronic effects, but can occur cleanly and stereoselectively (Eqs. 51[136] and 52[137]).[138−141] Among many recent synthetic applications,[142−148] two examples are shown in Eqs. 53[65] and 54.[147] Cyclopropyl ethers are considerably less reactive than the corresponding cyclopropanols.[125]



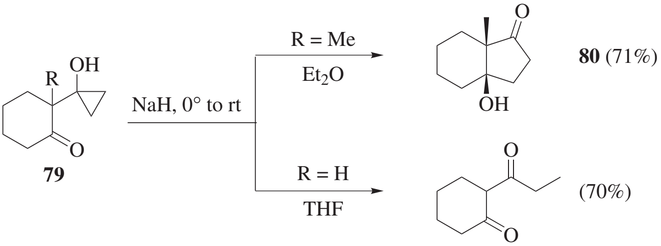
(Eq. 51)



(Eq. 52)

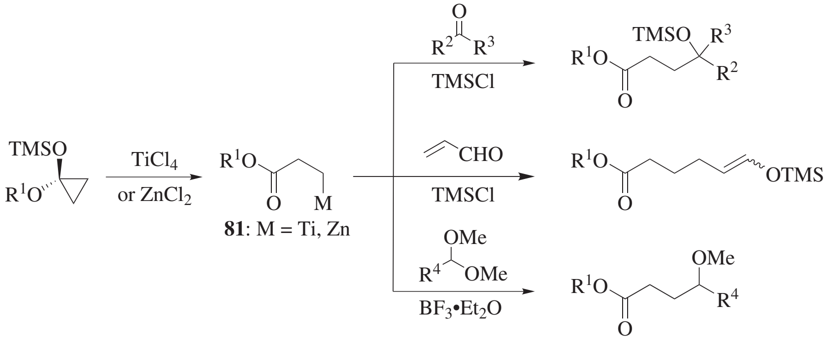


(Eq. 53)

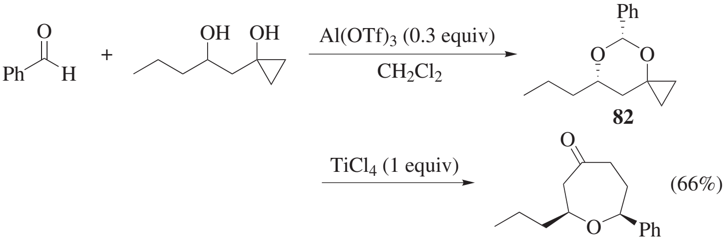


(Eq. 54)

Cyclopentanone annulation by means of a cyclopropanol, illustrated by the conversion of cyclopropanol derivative **79** to cyclopentanone **80** in Eq. 54, represents a successful intramolecular trapping of a homoenolate by a carbonyl group.[145–149] A general route to homoenolates entails treatment of a cyclopropanone hemiacetal with $TiCl_4$ or $ZnCl_2$ to generate the corresponding titanium or zinc homoenolate **81** (Scheme 16).[132] Several synthetically useful C−C bond forming reactions of **81** result from addition of suitable electrophiles, including carbonyl compounds, α,β-unsaturated carbonyl compounds, and acetals. Transmetallation of intermediate **81** broadens the scope.[132,150] In contrast, there are only a handful of related uses involving cyclopropanols.[52,151–153] Recent examples of intramolecular variants involve addition of cyclopropanols to oxocarbenium ion intermediates generated in situ from acetals such as **82** (Eq. 55)[52] and **83** (Eq. 56).[153]

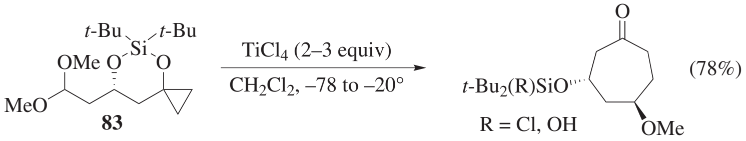


Scheme 16. Use of cyclopropanone hemiacetals as homoenolate precursors.



82

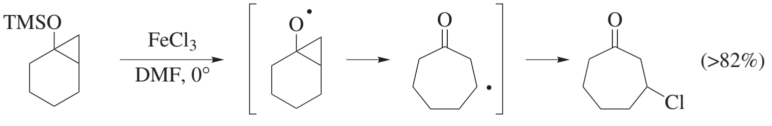
(Eq. 55)



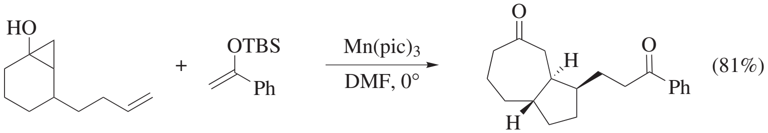
83

(Eq. 56)

Oxidative cleavage of cyclopropanols provides another method for C1–C2 scission and is induced by various one-electron oxidants such as Fe^{3+}, Ag^{+}, Cu^{2+}, Mn^{3+}, V^{5+}, and Cr^{4+}, as well as molecular oxygen, *tert*-butyl hydroperoxide, hypervalent iodine, and lead tetraacetate.[10,125,128,133,154] Siloxycyclopropanes also undergo homolytic cleavage by most of these oxidants. These reactions are likely to involve initial generation of the cyclopropoxy radical, leading to a β-keto radical. In accord with a free-radical mechanism, the more substituted C–C bond undergoes ring opening (Eq. 57[155]).[81,156] Attractive annulation procedures involve trapping β-acyl radical intermediates with pendant double or triple bonds,[157–163] as shown in Eq. 58,[161] where manganese(III) pyridine-2-carboxylate is used as the one-electron oxidant.

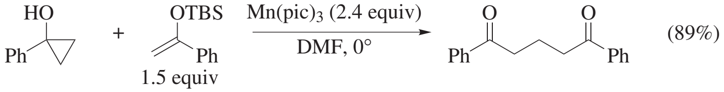


(Eq. 57)

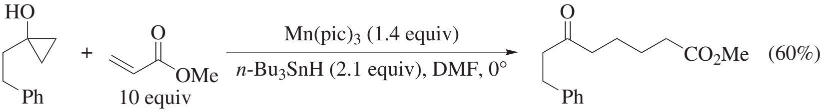


(Eq. 58)

This reagent is particularly effective in the intermolecular addition of cyclopropanols to alkenes (Eqs. 59[162] and 60[163]). It is interesting to note that $Mn(pic)_3$ is compatible with reducing agents, such as tributyltin hydride and diphenyl diselenide, which in turn allows use of electron-deficient alkenes as the radical acceptors. Other notable methods include the use of a catalytic amount of $AgNO_3$ with $(NH_4)_2S_2O_8$ as the stoichiometric oxidant[164,165] and free-radical-mediated preparation of 1,6-dicarbonyl compounds via β-keto organomercurial salts, which are readily available from mercuration of cyclopropanol silyl ethers.[166,167]

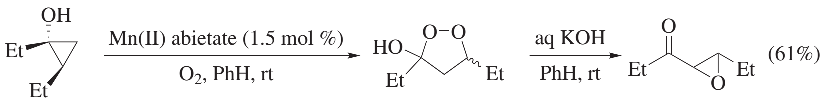


(Eq. 59)



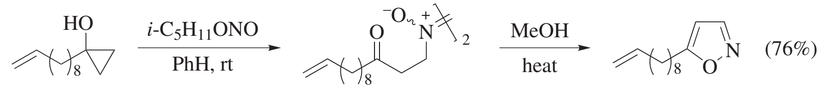
(Eq. 60)

Manganese-catalyzed oxidation of cyclopropanol **84** with oxygen gives cyclic peroxides that are cleanly converted into α,β-epoxyketone **85** by the action of base (Eq. 61).[168] Treatment of cyclopropanol **86** with *iso*-amyl nitrite affords the dimeric β-nitrosoketone, which provides 5-substituted isoxazole **87** upon heating in methanol (Eq. 62).[169]



84 **85**

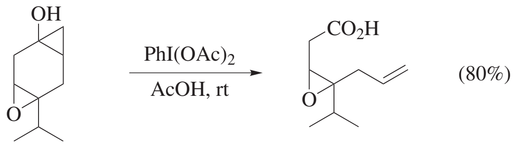
(Eq. 61)



86 **87**

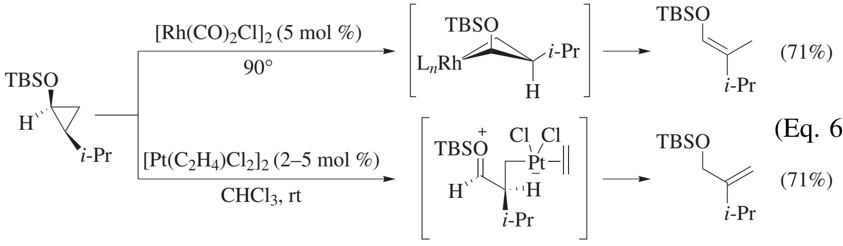
(Eq. 62)

Oxidation of cyclopropanols with lead(IV) acetate or (diacetoxy)iodobenzene results in scission of both C1−C2 and C2−C3 bonds (Eq. 63).[170,171]

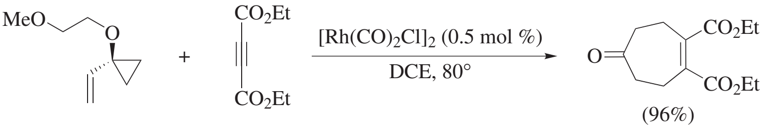


(Eq. 63)

Transition-metal-catalyzed isomerization of cyclopropanol derivatives affords allyl ethers and/or enol ethers, as shown in two representative examples (Eq. 64).[172,173] Both transformations take place stereospecifically. One spectacular application of transition-metal-catalyzed ring cleavage of a cyclopropanol derivative in a C−C bond forming reaction is the homo-Diels-Alder reaction for efficient assembly of seven-membered carbocycles (Eq. 65).[174] This useful method has been extensively developed for [5 + 2] cycloaddition reactions of vinylcyclopropanes.[175−177] Another transition-metal-catalyzed transformation involves arylative ring opening of siloxycyclopropanes with aryl triflates in the presence of a palladium(II) catalyst to afford β-aryl ketones and esters.[178,179]

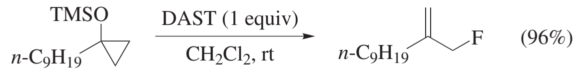


(Eq. 64)

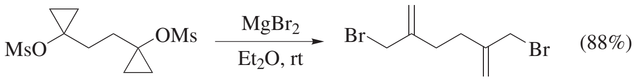


(Eq. 65)

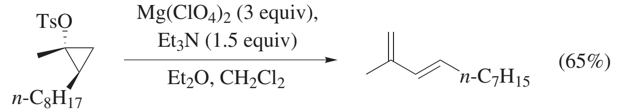
Solvolysis of cyclopropyl sulfonates or halides involves a concerted ionization/ring-opening process.[125,180,181] Recently, two procedures of preparative value involving C2−C3 ring opening have been developed. Treatment of tertiary cyclopropyl silyl ethers with diethylaminosulfur trifluoride (DAST) affords allylic fluorides in moderate to good yields (Eq. 66).[182,183] The cyclopropyl−allyl rearrangement of 1-alkylcyclopropyl sulfonates is accomplished by the action of a magnesium halide providing convenient access to 2-substituted allylic halides (Eq. 67[184]).[185] The corresponding *E*-dienes are obtained cleanly by employing magnesium perchlorate in place of magnesium halides (Eq. 68).[186]



(Eq. 66)

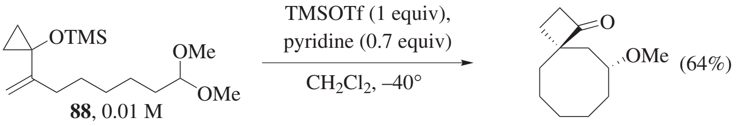


(Eq. 67)



(Eq. 68)

α-Vinylcyclopropanols have found extensive use in organic synthesis, as they undergo facile ring expansion into cyclobutanones via cyclopropylcarbinyl cation intermediates.[127,129,130,187–189] Addition of α-vinylcyclopropanol silyl ethers to oxocarbenium ions generated from acetals affords alkylated cyclobutanones in excellent yields.[129] The cyclization of cyclopropanol derivative **88** to the eight-membered carbocycle **89** without having to resort to high dilution is noteworthy (Eq. 69).[190]

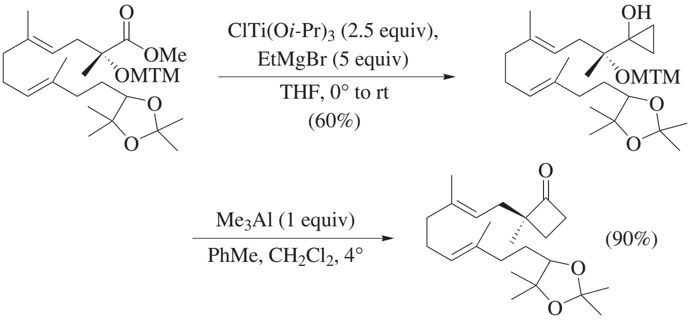


88, 0.01 M

89

(Eq. 69)

Related ring enlargement reactions of 1-(1-hydroxyalkyl)cyclopropanol derivatives (Eq. 70),[191] 1-(1-phenylselenoalkyl)cyclopropanols, and oxaspiropentanes are also reported for the stereoselective preparation of cyclobutanones.[46,129,191–194]

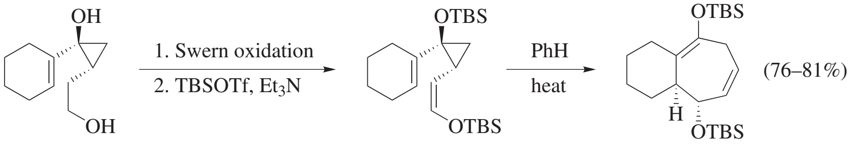


(Eq. 70)

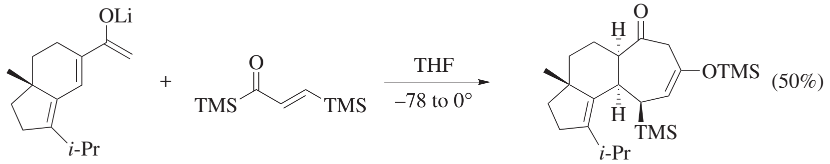
Rearrangement of 1-(1-alkynyl)cyclopropanols to 2-cyclopenten-1-ones is induced by complexation of the alkynyl moiety with $Co_2(CO)_8$ and proceeds catalytically by the addition of a triaryl phosphite as a ligand.[195–197] Either 5-substituted or 4-substituted 2-cyclopenten-1-ones can be prepared selectively by a judicious choice of a protecting group of the cyclopropanol and the configuration of substituents. The reaction mechanism is believed to be analogous to that of the Pauson-Khand reaction.

The vinylcyclopropane-cyclopentene rearrangement has seen frequent synthetic applications. In addition to thermolysis, catalysis by a transition metal has recently been reported.[198] A remarkably facile vinylcyclopropane rearrangement takes advantage of alkoxy-acceleration. Thus, the lithium salt of 2-vinylcyclopropanol rearranges to 3-cyclopentenol at room temperature.[199,200]

Cyclopropanol derivatives are also utilized for the oxy-Cope rearrangement of *cis*-divinylcyclopropanes, which lead to the convenient construction of seven-membered carbocycles (Eq. 71).[201] An anionic oxy-Cope version has also been developed by means of the Brook rearrangement (Eq. 72).[202,203]

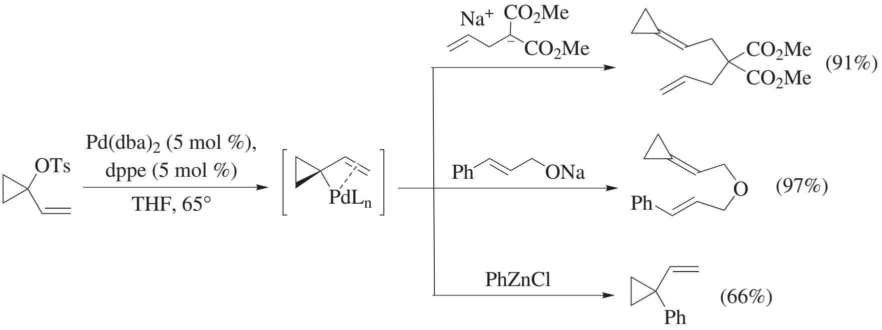


(Eq. 71)



(Eq. 72)

Also known is the elaboration of cyclopropanone hemiacetals and cyclopropanol derivatives with retention of the cyclopropane ring. For example, the Strecker reaction of cyclopropanone hemiacetals gives a precursor to amino cyclopropanecarboxylic acids.[204] Formation of π-allylpalladium intermediates from 1-alkenylcyclopropyl sulfonates is readily accomplished by catalytic amounts of palladium(0). Subsequent Pd(0)-catalyzed substitution reactions proceed with excellent regioselectivity, depending on the nature of the nucleophiles (Scheme 17).[205,206]

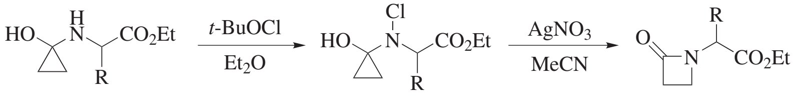


Scheme 17. Generation and reactions of π-allylpalladium intermediates.

Cyclopropanols can be readily converted into cyclopropylidene derivatives, the synthetic utility of which has long been established.[207–210] An interesting general approach to bicyclopropylidenes and triangulanes employs the Kulinkovich cyclopropanation of cyclopropanecarboxylates.[211]

Applications of Aminocyclopropanes

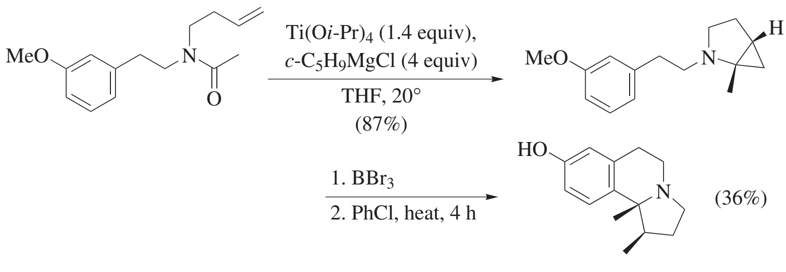
Primary aminocyclopropanes undergo smooth ring opening upon exposure to base, but are inert to acid hydrolysis due to rapid formation of the strongly deactivating ammonium salts.[133–135] Tertiary aminocyclopropanes resist ring cleavage by acids, bases, or electrophiles. Thus, early work has been directed primarily at applications of primary and secondary aminocylopropanes. Ring expansion of 1-(chloroamino)cyclopropanols (Eq. 73),[212] which are readily available by the action of *tert*-butyl hypochlorite on aminocyclopropanes, affords higher yields of β-lactams than the reaction of 1-alkoxycyclopropanols with sodium azide.[126]



R	Yield (%)
Bn	70
4-$MeOC_6H_4$	52

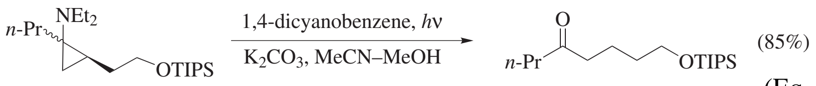
(Eq. 73)

Thermolysis of tertiary aminocyclopropanes is known to cause ring scission. The resulting iminium ion intermediates may be trapped by an electron-rich aromatic tether resulting in an intramolecular Friedel-Crafts alkylation (Eq. 74).[213]

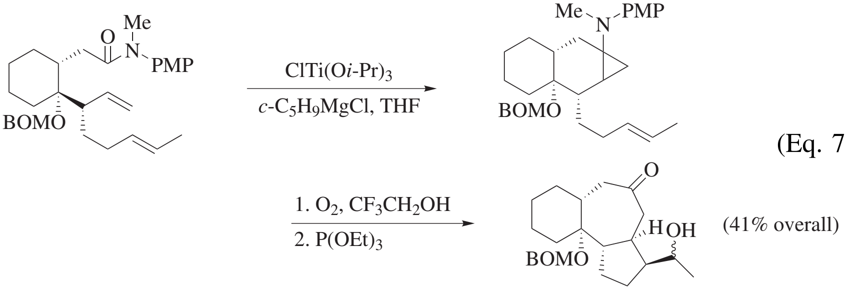


(Eq. 74)

Facile ring opening of aminocyclopropanes is achieved under mild conditions via radical-cation intermediates (Eq. 75[214]).[215–217] The requisite species can be conveniently generated by photooxidation of tertiary aminocyclopropanes. The overall transformation is analogous to the well-known cyclopropylcarbinyl–homoallyl radical rearrangement. This one-electron oxidation protocol has been extended to [3 + 2] cycloadditions and construction of medium-sized carbocycles by tandem application of 5-exo radical cyclizations.[215,216] It is interesting to note that the use of the *p*-anisidine *N*-substituent makes possible aerobic oxidation of tertiary aminocyclopropanes and also increases diastereoselectivity of the 5-*exo* radical cyclization step (Eq. 76).[216]



(Eq. 75)

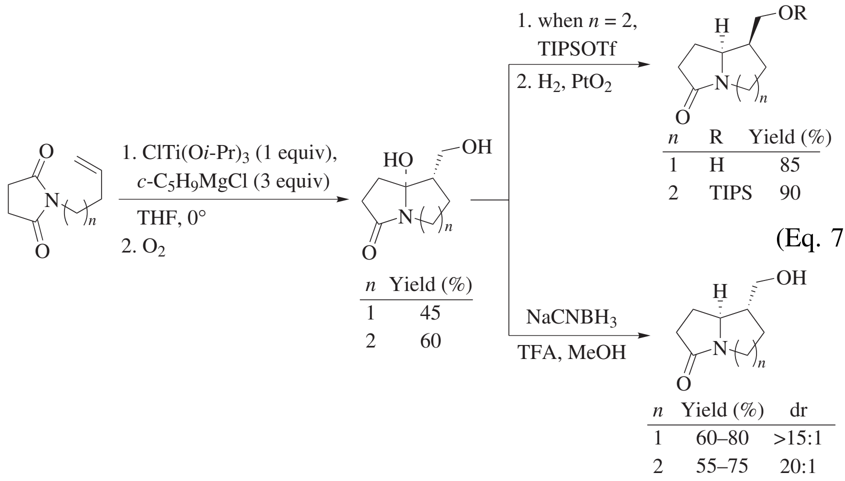


(Eq. 76)

Formation of aminium radicals and subsequent ring opening are also implicated in the inactivation of cytochrome P-450 and monoamine oxidase by cyclopropylamines.[218–220] Also related is the oxidative conversion of 1-aminocyclopropanecarboxylic acid into ethylene, cyanide, and carbon dioxide in plants.[221–223]

Applications of Imides

As exemplified by Eq. 48, the titanium-mediated cyclization of vinyl-tethered imides provides a new and convenient route to *N*-acyl hemiaminals, which serve as the most commonly utilized precursors to *N*-acyliminium ions. The utility of these ions has been amply demonstrated in the stereoselective syntheses of a wide range of structurally diverse nitrogen heterocycles.[108–111] The present method complements other reliable procedures for preparing *N*-acyl hemiaminals that involve reduction of imides or *N*-acyl lactams, and α-oxidation of primary or secondary amides.[224] Stereocontrolled reduction of the *N*-acyl hemiaminal moiety to either stereoisomer has been accomplished by employing catalytic hydrogenation or treatment with $NaCNBH_3$ (Eq. 77).[225]



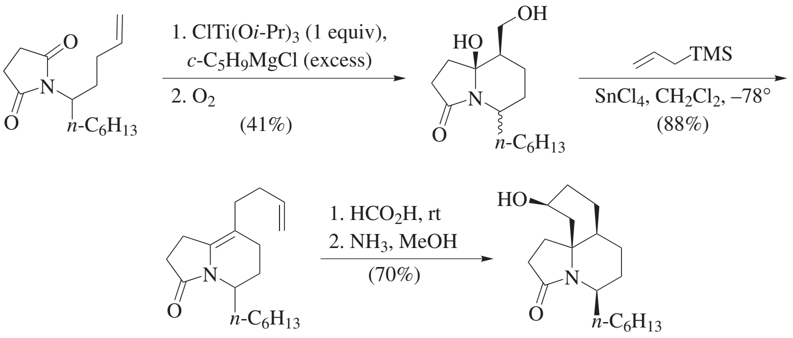
n	Yield (%)
1	45
2	60

n	R	Yield (%)
1	H	85
2	TIPS	90

(Eq. 77)

n	Yield (%)	dr
1	60–80	>15:1
2	55–75	20:1

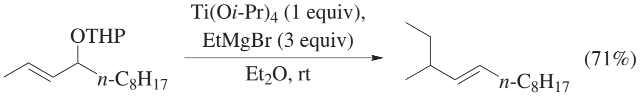
Ready access to tertiary *N*-acyliminium ions is another distinctive feature of the present method. Tertiary *N*-acyl hemiaminals undergo both inter- and intramolecular C–C bond-forming reactions, as shown in the diastereoselective construction of the lepadiformine framework (Eq. 78).[106] Tertiary *N*-acyl hemiaminals may also be utilized for a Nazarov cyclization.[107,226] These *N*-acyl hemiaminals are obtained typically in moderate yields, but recent studies indicate that use of Ti(O*i*-Pr)$_4$–2 *n*-BuLi[24] could improve the yields of this reaction.[227]



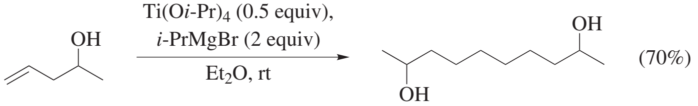
(Eq. 78)

Other Applications of Dialkoxytitanacyclopropanes

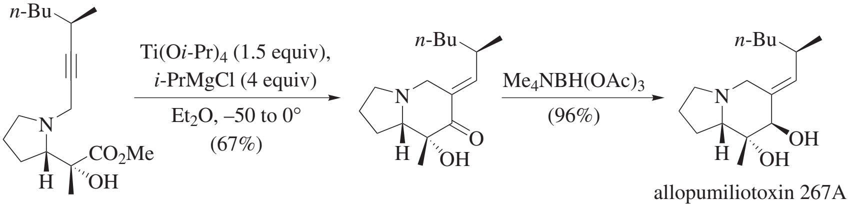
This chapter has focused on the cyclopropanation reactions and closely related transformations of carboxylic acid derivatives. The pivotal Kulinkovich intermediates, diisopropoxytitanacyclopropanes [Ti(O*i*-Pr)$_2$(η^2-alkene)], have also proved to be versatile for accomplishing other types of intermolecular C–C bond-forming transformations (Eqs. 79[40] and 80[228]). Functionalized allyl, propargyl, or allenyltitanium reagents can be readily generated in situ by the action of diisopropoxytitanacyclopropanes on allyl or propargyl alcohol derivatives for subsequent addition to suitable electrophiles. A new class of particularly useful intermediates arises from [Ti(O*i*-Pr)$_2$(η^2-alkyne)]. These alkyne complexes readily react with various electrophiles, including olefins (carbometallation). Many synthetic applications are known, some of which broaden the scope of the well-known chemistry of titanocene ("Cp$_2$Ti") or zirconocene reagents ("Cp$_2$Zr"), as illustrated in Eq. 81.[229–231] The readers are referred to several excellent reviews on these useful transformations.[5–9] These intermediates are also utilized in the preparation of aromatic carbocycles and heterocycles.[232,233] More recent applications include attractive methods for acyclic stereoselection by taking advantage of the directing effects of allylic, homoallylic, and homopropargylic alcohols.[64,65,74,104,105,234,235]



(Eq. 79)



(Eq. 80)



allopumiliotoxin 267A

(Eq. 81)

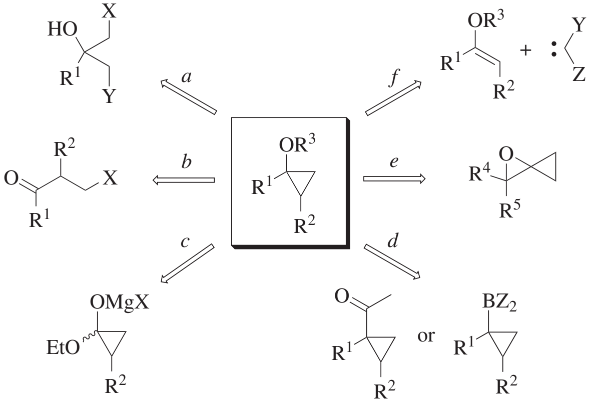
COMPARISON WITH OTHER METHODS

Many methods are available for the preparation of heteroatom-substituted cyclopropanes. These transformations have been extensively reviewed;[10,11,113,114,120–135,236] only a brief summary of the more frequently used synthetic procedures is presented here. Because of the wide diversity of the known methods, it is difficult to make direct comparisons. It seems appropriate to start with the most attractive features of the Kulinkovich cyclopropanation, which are its experimental simplicity and the fact that it employs readily available and inexpensive starting materials (i.e., titanium isopropoxide, Grignard reagents, carboxylic acid derivatives, and olefins). Thus, no extra steps are required to prepare the appropriate precursors. A related advantage is that one can employ similar reaction conditions in the cyclopropanation reactions to prepare different heteroatom-substituted cyclopropanes from the respective carboxylic acid derivatives such as esters, amides, nitriles, and carbonates. High *cis*-dialkyl diastereoselectivity observed for cyclopropanation of unbranched esters also plays an important role in the synthetic applications.

Among common heteroatom-substituted cyclopropanes, alkylthio- and halocyclopropanes[237–239] are inaccessible by the Kulinkovich cyclopropanation. This section is focused on the syntheses of cyclopropanols and cyclopropylamines. With regard to limitations of the Kulinkovich cyclopropanation, the most conspicuous facets are a paucity of generally applicable protocols for enantioselective cyclopropanations and the fact that highly substituted cyclopropanes are typically inaccessible. A handful of notable exceptions notwithstanding, the Kulinkovich reaction is limited primarily to preparation of heteroatom-substituted cyclopropanes containing one or two alkyl groups.

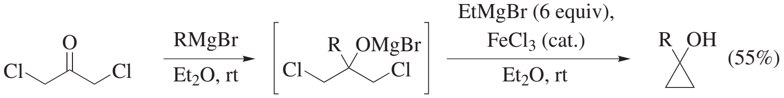
Preparation of Cyclopropanols

Preparative methods for cyclopropanols include: 1,3-elimination (path *a*), cyclization of β-oxo carbanion equivalents (path *b*), alkylation of cyclopropanone hemiacetals (path *c*); elaboration of functionalized cyclopropanes (path *d*), elaboration of oxaspiropentanes (path *e*), and carbenoid cyclopropanation of enol ethers and derivatives (path *f*) (Scheme 18).



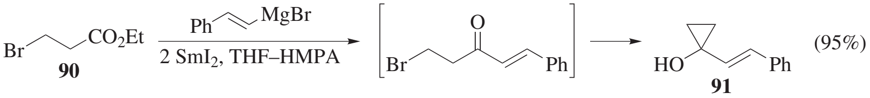
Scheme 18. Representative methods for preparing cyclopropanols and derivatives.

Considering that the formation of three-membered rings is entropically favorable, it is not surprising that a classic approach is based on 1,3-ring closure: 1-alkyl-substituted cyclopropanols are prepared in moderate yields by treatment of the magnesium salts of 1,3-dihalo-2-propanols with a Grignard reagent in the presence of ferric chloride (Scheme 18, path *a*) (Eq. 82).[240] A related approach involves the treatment of acid chlorides with chloromethyllithium.[241] It does not appear that this method has been extended to the preparation of more highly substituted cyclopropanols.



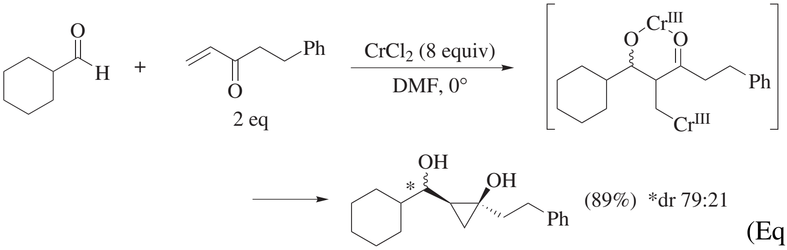
(Eq. 82)

An alternative mode of cyclization involves use of β-oxo carbanionic equivalents to afford cyclopropanols (Scheme 18, path *b*).[242] A wide array of substrates are suitable for 1,3-closure; reductive cyclization of β-halo aldehydes and ketones has been frequently used by means of suitable reducing agents such as Zn, In, SmI_2, etc.[145,146,243–247] Thus, addition of one equivalent of a Grignard reagent to ester **90** in the presence of SmI_2 affords cyclopropanol **91** in excellent yield (Eq. 83).[244] β-Stannyl and β-silyl carbonyl compounds also undergo cyclization under appropriate conditions to generate cyclopropanols.[248,249] Early examples include hydroboration of propargyl bromide,[250] Clemmensen reduction of 1,3-diketones (for formation of *vic*-cyclopropanediols),[251] addition of a carbanion (generated in situ by reduction of α,β-unsaturated enones) to a pendant ketone,[252] and photolysis of 3-morpholinopropiophenones.[253,254]



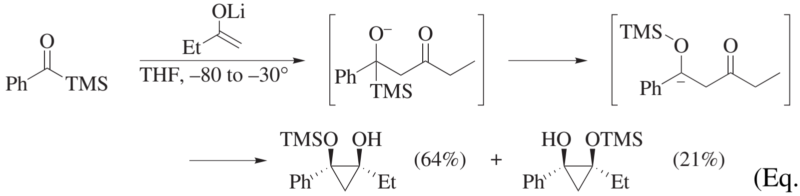
(Eq. 83)

A recent useful variant involves reduction of α,β-unsaturated aldehydes or ketones with CrCl$_2$. In these reactions water is necessary to induce the cyclopropanol formation.[255,256] The identical procedure has been successfully extended to cross-coupling of α,β-unsaturated ketones and aliphatic aldehydes, in which a *trans*-1,2-dialkyl configuration is consistent with chelation of Cr(III) to the alkoxy and carbonyl groups (Eq. 84).[256,257] This method is tolerant of α-substituents in α,β-unsaturated carbonyl compounds, thus providing easy access to 1,2,2-trisubstituted cyclopropanols. However, the presence of β-substituents is detrimental.



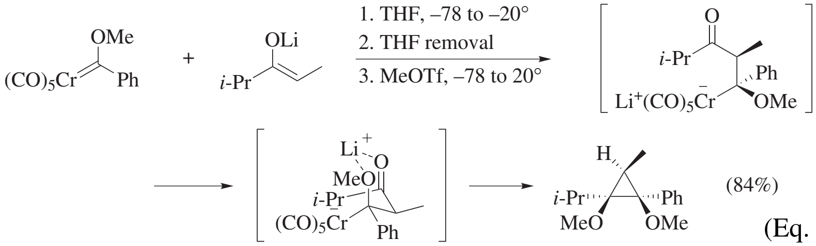
(Eq. 84)

A conceptually attractive approach makes use of a Brook rearrangement. Addition of a ketone enolate to an acylsilane is accompanied by a Brook rearrangement and subsequent cyclization to provide a functionalized cyclopropanol with high stereoselectivity (Eq. 85).[151,202,203,258]



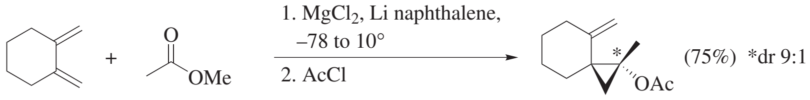
(Eq. 85)

A diastereoselective synthesis of highly substituted cyclopropanols is reported by direct combination of a Fischer carbene complex with ketone lithium enolates (Eq. 86).[259]



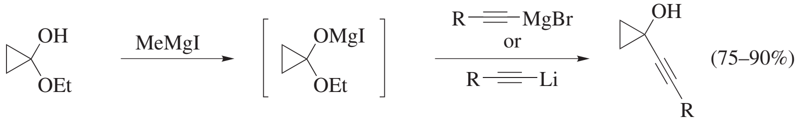
(Eq. 86)

Cathodic reduction of mixtures of styrenes and esters with a magnesium electrode gives 2-phenylcyclopropanols as single isomers.[260] Treatment of the magnesium complexes of 1,2-bis(methylene)cyclohexane with esters at low temperature also gives cyclopropanols (Eq. 87).[261] Although no mechanistic study is reported, it is presumed that both transformations are analogous to the Kulinkovich cyclopropanation.



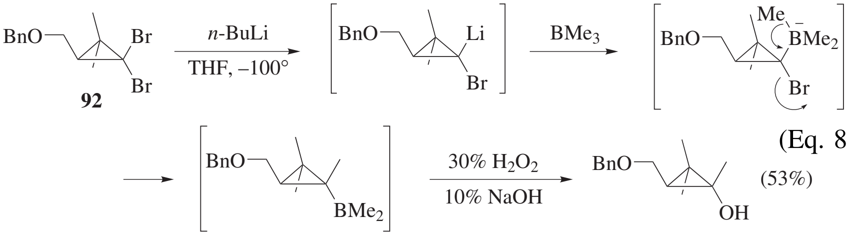
(Eq. 87)

Another convenient method involves reactions of the magnesium salts of cyclopropanone hemiacetals with nucleophiles (Scheme 18, path *c*).[127,130,262] This approach owes much to the well-established preparation and high reactivity of cyclopropanone hemiacetals (see below) and is particularly useful for the preparation of 1-alkenyl- and 1-alkynylcyclopropanols (Eq. 88).[130,206] Ring contraction of cyclobutanone derivatives to prepare cyclopropanols or their ethers is also known.[263–265]



(Eq. 88)

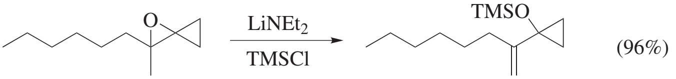
An obvious route to cyclopropanols involves functionalization of cyclopropanes, which is predicated on the availability of three-membered ring compounds (Scheme 18, path *d*). The Baeyer-Villiger oxidation of methyl cyclopropyl ketones gives cyclopropyl acetates.[266] Because of the well-known migratory aptitude of alkyl groups in Baeyer-Villiger oxidations, this approach is limited primarily to the methyl ketones to preclude exclusive formation of the corresponding cyclopropanecarboxylates. Highly substituted cyclopropanols are available from oxidation of cyclopropylborane or -boronic acid derivatives. The requisite intermediates are prepared stereoselectively by employing 1,1-dibromocyclopropanes such as **92** (Eq. 89).[267] An alternate method involves cyclopropanation of 1-alkenylboronic acids, which can be achieved enantioselectively.[268,269] Another preparation of cyclopropanols is the Kumada-Tamao-Fleming oxidation of cyclopropylsilanes, in which a silicon moiety, such as allyldimethylsilyl or silanol functionality, is employed as a latent hydroxyl group.[270–272]



92

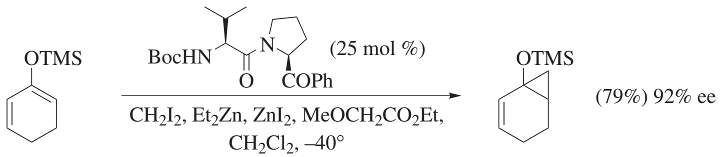
(Eq. 89)

A versatile method for making cyclopropanols starts from oxaspiropentanes (Scheme 18, path *e*), which are prepared by several convenient methods, including use of diphenylsulfonium cyclopropylide.[129,273,274] This attractive method would seem to be applicable to more highly substituted cyclopropyl sulfur ylides, but to date, such an extension has not been reported. This reliable procedure is particularly convenient for the preparation of 1-alkenylcyclopropanols (Eq. 90),[274] which are often difficult to obtain in satisfactory yields by the Kulinkovich cyclopropanations of α,β-unsaturated esters.



(Eq. 90)

The most frequently used method for preparing highly substituted cyclopropanol derivatives is the Simmons-Smith reaction of enol esters and silyl enol ethers and related reactions with carbenoids generated by transition-metal-catalyzed decomposition of diazoalkanes (Scheme 18, path *f*).[275–278] Several modifications have been developed, including treatment of ketone enolates with CH_2I_2–SmI_2 for direct preparation of free cyclopropanols.[279–282] Impressive advances have been made recently in the use of asymmetric carbenoid cyclopropanation reactions (Eq. 91)[283] to prepare enantiomerically enriched cyclopropanes and cyclopropanols.[283–286]



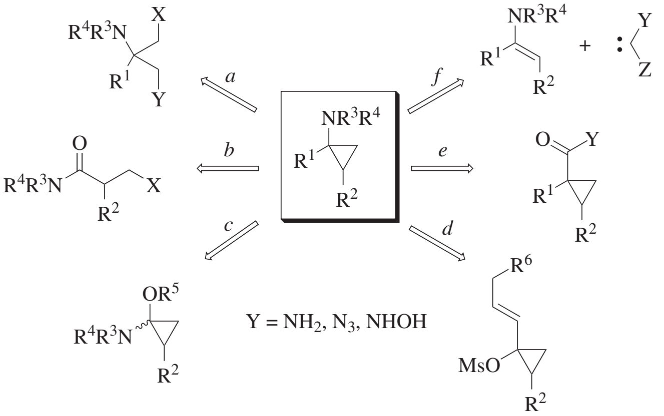
(Eq. 91)

Preparation of Cyclopropanone Hemiacetals

A most convenient and flexible route to 1-siloxy-1-alkoxycyclopropanes is the cyclization of β-halo carboxylic acid derivatives.[126,127,130,287] Sonication or the use of TMSCl and SmI_2 improves the efficacy of this reliable method.[245,288] The parent cyclopropanone and alkyl-substituted cyclopropanones are prepared in 60–90% yield by the diazoalkane–ketene reaction.[126] Most cyclopropanones are not isolable, but instead are obtained as the hydrates or hemiacetals by addition of water or alcohols. The Simmons-Smith cyclopropanation of silyl ketene acetals provides another useful method.[276,289–291]

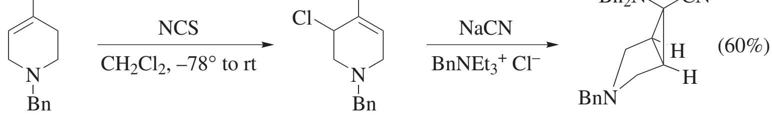
Preparation of Aminocyclopropanes

The known methods for preparing aminocyclopropanes parallel those for cyclopropanols (Scheme 18). As shown in Scheme 19, they include: 1,3-elimination (path *a*), cyclization of β-acylcarbanion equivalents (path *b*), alkylation or reduction of cyclopropyl aminals (path *c*); elaboration of alkylidenecyclopropanes and derivatives (path *d*), the Hoffmann, Curtius, and Lossen rearrangements of cyclopropanecarboxylic acid derivatives (path *e*), and cyclopropanation of enamine derivatives with carbenoids (path *f*). Detailed discussions of these and other less frequently used methods can be found in a comprehensive review.[135]

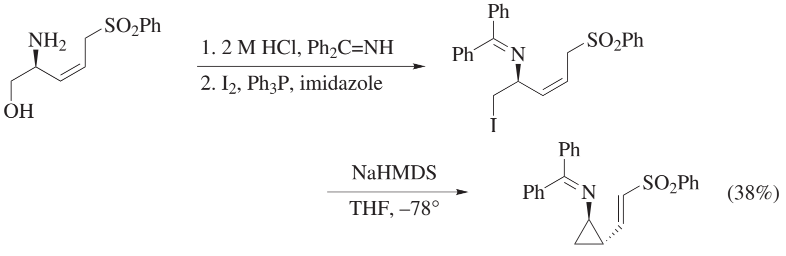


Scheme 19. Representative methods for preparing aminocyclopropanes.

1,3-Cyclization procedures (Scheme 19, path *a*) are used frequently for preparation of cyclopropylamines (Eq. 92[292]).[293,294] The bicyclic iminium ion intermediates can be trapped by nucleophiles other than cyanide, such as hydrides[295] and alkyl groups (by means of dimethylzinc, alkylcuprates, or Grignard or organolithum reagents in the presence of TMEDA),[296] to furnish the corresponding cyclopropylamines. Similarly, the Favorskii-type rearrangment of α-halo ketimines gives cyclopropylamine derivatives.[297] Electrochemical oxidation of enamines in a KI–NaCN–MeOH system gives cyclopropanone *N*,*O*-acetals, which serve as useful precursors to the bicyclic iminium ions.[298] A straightforward variant entails S_N2-alkylation by utilizing amino nitriles derived from β-chloro aldimines and benzylideneglycinates. These procedures provide convenient routes to 1-aminocyclopropane-1-carboxylic acid derivatives.[299,300] Lithiation–cyclization of *N*-Boc chloroalkyl secondary amines also provides a convenient synthesis of 3-, 5- and 6-membered nitrogen heterocycles.[301] An allylic sulfone is used to initiate 1,3-cyclization to prepare a functionalized cyclopropylamine (Eq. 93).[302]

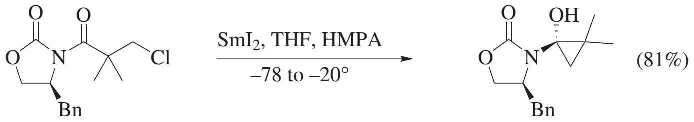


(Eq. 92)



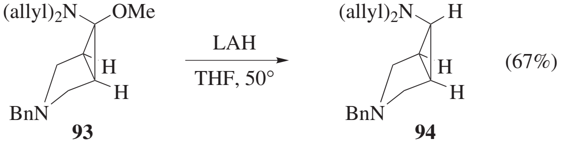
(Eq. 93)

In recent examples of cyclization of β-acylcarbanion equivalents (Scheme 19, path *b*), SmI_2-mediated ring closure is utilized to prepare enantiomerically pure cyclopropanone hemiaminals (Eq. 94).[245]



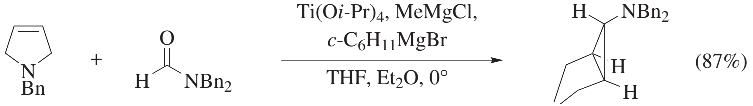
(Eq. 94)

By analogy to the previously mentioned reactions of cyclopropanone hemiacetals with nucleophiles, the cognate substitution reactions of cyclopropylaminals with various nucleophiles are frequently utilized (Scheme 19, path *c*).[292,294–298,303] Thus, reduction of cyclopropyl aminal **93** with $LiAlH_4$ affords cyclopropylamine **94** (Eq. 95).[294,304] The Kulinkovich cyclopropanation of 3-pyrroline **95** proceeds with the opposite diastereofacial selectivity to give amine **96** (Eq. 96).[82] It is interesting to note that five-membered cycloalkenes such as cyclopentene or 3-pyrrolines are rare examples of disubstituted olefins that undergo the Kulinkovich cyclopropanation with amides in good yields.



93 **94**

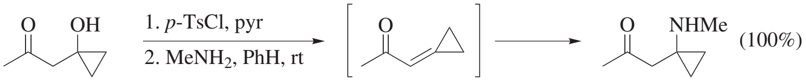
(Eq. 95)



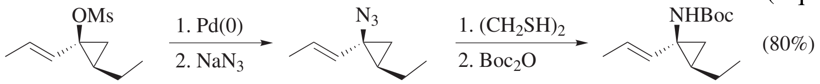
95 **96**

(Eq. 96)

Functional group manipulation of cyclopropane derivatives also provides convenient routes to cyclopropylamines (Scheme 19, path *d*). For example, a cyclopropanol function, which is available by the Kulinkovich cyclopropanation of esters, can be readily elaborated by a judicious placement of a carbonyl group to allow in situ formation of a conjugated cyclopropylidene ketone (Eq. 97).[305] Pd(0)-catalyzed substitution reactions of 1-alkenylcyclopropyl sulfonates proceed via the corresponding π-allylpalladium intermediates with retention of the three-membered ring and with excellent regioselectivity, depending on the nature of the nucleophile. Use of an azide gives a new, convenient route to functionalized cyclopropylamines (Eq. 98[37]).[205,206]

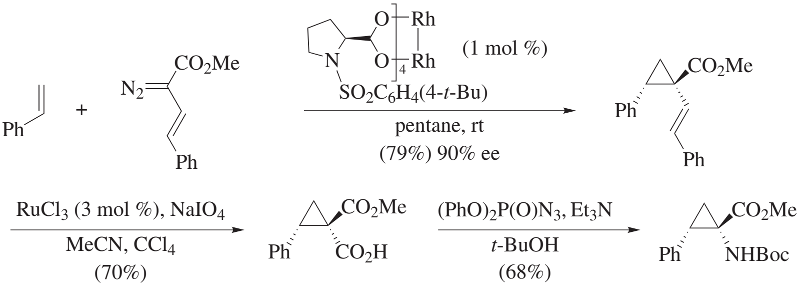


(Eq. 97)



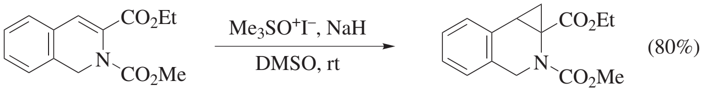
(Eq. 98)

Among the most frequently used methods for the preparation of cyclopropylamines are the Hofmann, Curtius, and Lossen rearrangements of cyclopropanecarboxylic acid derivatives (Scheme 19, path *e*). This approach is versatile, especially because these precursors are readily available by cyclopropanation using diazoacetates and related compounds. As shown in Eq. 99,[306] recent studies are directed at enantioselective reactions.[307]

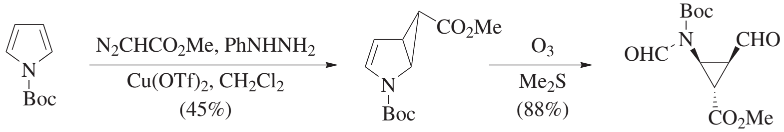


(Eq. 99)

Cyclopropanation of enamine derivatives with carbenoids (dihalocarbenes, the Simmons-Smith reagent, diazoalkanes, dimethylsulfonium methylides, pyridinium ylides, etc.) are also widely used for the preparation of cyclopropylamines (Scheme 19, path *f*). The presence of an electron-withdrawing group such as an ester allows use of a wide range of carbenoid reagents, which can react by way of Michael reactions.[120,135] Selected examples are shown in Eqs. 100[308] and 101[309–314] and the readers are referred to comprehensive reviews.[120,135]

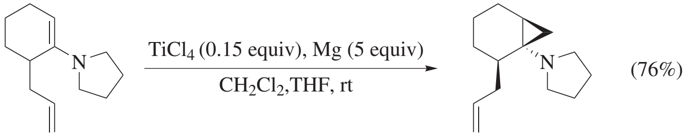


(Eq. 100)



(Eq. 101)

An expedient method for generating titanium carbenoids in situ employs the CH_2Cl_2–$TiCl_4$–Mg reagent. The presumed titanium-methylene complex is effective for methylenation of aldehydes, ketones, and esters.[315] This reagent also reacts with enamines to give the corresponding cyclopropylamines in good yields (Eq. 102).[316] Formation of the titanacyclobutane intermediate from the Fisher-type titanium–methylene complex and the enamine double bond, and subsequent reductive elimination are presumed to account for the cyclopropanation. This convenient procedure has been extended to tandem methylene transfer reactions of amides for chemoselective preparation of cyclopropylamines in moderate to good yields.[317]

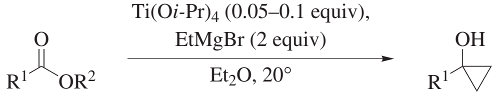


(Eq. 102)

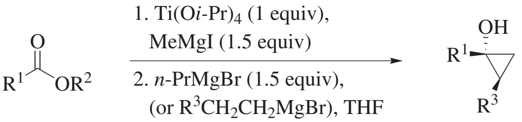
EXPERIMENTAL CONDITIONS

Kulinkovich reactions are carried out in conventional apparatus under an inert (nitrogen or argon) atmosphere. Use of a syringe pump is most convenient for slow addition of a Grignard reagent. Otherwise, no special equipment or handling is necessary. If the reaction is done on a large scale, *it is very important that appropriate precautions are made to deal with evolution of the alkane gas* derived from the Grignard reagent such as ethane or butane when ethyl or butyl Grignard reagents are employed.

EXPERIMENTAL PROCEDURES

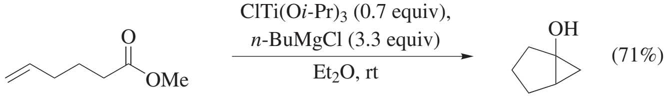


General Procedure for Catalytic Cyclopropanation Reactions of Esters: Preparation of Cyclopropanols.[2] To a stirred solution of a carboxylic ester (25 mmol) and Ti(O*i*-Pr)$_4$ (0.74 mL, 2.5 mmol) in Et$_2$O (80 mL) was added slowly over 3 h at 18–20° a solution of ethylmagnesium bromide (53 mmol) in Et$_2$O (60 mL). The reaction mixture was stirred for 10 min, poured into cooled (5°) 10% H$_2$SO$_4$ solution (250 mL), and then extracted with Et$_2$O (3 × 50 mL). The combined organic layers were washed with water (50 mL) and dried (Na$_2$SO$_4$). The solvent was removed under reduced pressure. The cyclopropanol products were purified by distillation or column chromatography on silica gel. For example, 1-*n*-amyl-1-cyclopropanol was obtained in 94% yield from methyl *n*-hexanoate: bp 82–83° (19 mm Hg); IR (CCl$_4$) 3600, 3320, 3080 cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$) δ 0.25–0.30 (m, 2H), 0.45–0.60 (m, 2H), 0.80 (t, 3H), 1.10–1.40 (m, 8H), 3.85 (br s, 1H, OH). Anal. Calcd for C$_8$H$_{16}$O: C, 74.94; H, 12.57. Found: C, 74.71; H, 12.74.

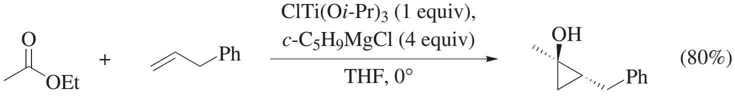


General Procedure for Stoichiometric Cyclopropanation Reactions of Esters: Preparation of *cis*-1,2-Disubstituted Cyclopropanols.[34] A 1.5 M solution of methylmagnesium iodide in ether or methylmagnesium bromide in

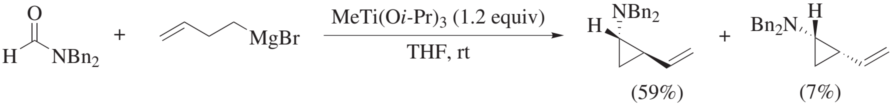
THF (20 mL, 30 mmol) was added within 5 minutes at room temperature to a solution of $\mathrm{Ti(O}i\text{-}\mathrm{Pr)_4}$ (5.68 g, 20 mmol) in 20 mL of $\mathrm{Et_2O}$ or THF. The resulting yellow or orange solution was cooled to 0° and a carboxylic ester (20 mmol, in 10 mL of $\mathrm{Et_2O}$ or THF) was then added. *n*-Propylmagnesium bromide or a higher homolog Grignard reagent (20–23 mL of a 1.5 M solution in $\mathrm{Et_2O}$ or THF; 30–35 mmol) was added over 30–40 min. The resulting reaction mixture was allowed to warm to room temperature, and then was stirred for an additional hour, quenched at 0° by careful addition of 10% aqueous sulfuric acid (70–80 mL), and extracted with $\mathrm{Et_2O}$ (3 × 20 mL). The combined organic layers were washed with saturated aqueous $\mathrm{NaHCO_3}$ and brine, dried over $\mathrm{Na_2SO_4}$ or $\mathrm{MgSO_4}$, and concentrated under reduced pressure. The products were purified by column chromatography over silica gel (petroleum ether/EtOAc). Secondary alcohols such as **22** (Eq. 11) were obtained as main byproducts. For example, *cis*-1-amyl-2-methyl-1-cyclopropanol was obtained in 75% yield from methyl hexanoate, *n*-propylmagnesium bromide, methylmagnesium bromide, and titanium(IV) isopropoxide in THF: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) δ −0.01–0.05 (m, 1H), 0.75–0.85 (m, 1H), 0.90 (t, $J = 6.9$ Hz, 3H), 1.01 (d, $J = 1.8$ Hz, 3H), 0.98–1.10 (m, 1H), 1.23–1.40 (m, 4H), 1.47–1.60 (m, 4H), 1.82 (br s, 1H, OH);^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$) δ 14.0, 14.2, 19.6, 20.6, 22.7, 25.5, 32.0, 33.9, 58.8. Anal. Calcd for $\mathrm{C_9H_{18}O}$: C, 76.00; H, 12.76. Found: C, 75.65; H, 12.43.



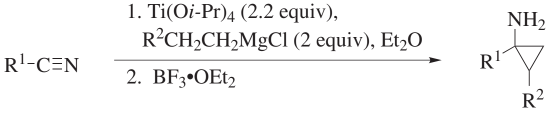
Bicyclo[3.1.0]hexan-1-ol (Typical Procedure for Intramolecular Cyclopropanation Reactions of Esters with Tethered Olefins). This procedure is described in *Organic Syntheses*.[318]



1*R,2*R**-2-Benzyl-1-methylcyclopropan-1-ol (Typical Procedure for Intermolecular Cyclopropanation Reactions of Esters with Monosubstituted Olefins).** This procedure is described in *Organic Syntheses*.[318]



***N*,*N*-Dibenzyl-*N*-(2-ethenylcyclopropyl)amine (Typical Procedure for Cyclopropanation Reactions of Carboxamides).** This procedure is described in *Organic Syntheses*.[319]



General Procedure for the Titanium-Mediated Cyclopropanation of Nitriles with Addition of a Lewis Acid to Give Cyclopropylamines.[92] To a solution of a nitrile (2 mmol) in ether (6 mL) were added sequentially at room temperature $Ti(O\textit{i}\text{-}Pr)_4$ (0.65 mL, 2.2 mmol) and a Grignard reagent (4 mmol of a 1 or 2 M solution in ether). After the mixture had been stirred for 30 min, $BF_3{\bullet}OEt_2$ (0.51 mL, 4 mmol) was added in one portion. The resulting mixture was stirred for an additional 10 min. A 10% solution of NaOH (ca. 1 mL) was added, and the mixture was extracted with ether. The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel. For example, 1-(2-benzyloxyethyl)cyclopropylamine was obtained in 54% yield from 3-benzyloxypropionitrile and ethylmagnesium bromide: IR (neat) 3357, 2857, 1454 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.43–0.46 (m, 2H), 0.56–0.59 (m, 2H), 1.69 (s, 2H, NH_2), 1.74 (t, $J = 6.3$ Hz, 2H), 3.69 (t, $J = 6.3$ Hz, 2H), 4.52 (s, 2H), 7.29–7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 33.1, 40.0, 69.1, 73.1, 127.6, 127.8, 128.4, 138.4; MS (Cl^+, NH_3) m/z: [M + 1] 192 (1), 106 (9), 84 (100).

TABULAR SURVEY

The tabular survey covers the literature reported through June 2008, but some recent additional references have been added. The tables are arranged in the order of the section on Scope and Limitations. The entries within each table are arranged in order of increasing carbon number of the starting carboxylic acid derivatives. Protecting groups are included in the carbon count.

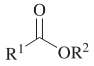
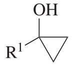
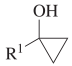
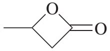
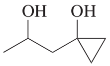
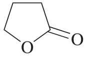
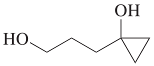
Lactones are covered in Tables 1 and 3, and cyclic carbonates in Tables 3 and 4. Acyl derivatives bearing oxazolidinones and Oppolzer's sultam are treated as esters, as their reactions with dialkoxytitanacyclopropane intermediates afford the cyclopropanol products. These examples thus appear in Tables 3 and 4.

The yields for the reactions are given in parentheses, followed by the ratio of diastereomers where applicable. Reaction times are not given in the tables, because the reactions are complete upon (slow) addition of the Grignard reagents or, if applicable, upon warming the reaction mixture to the indicated temperature.

The following abbreviations, which are not included in the *Journal of Organic Chemistry* list of standard abbreviations, are used in the tables:

BOM	benzyloxymethyl
eq	equivalents
MTM	methylthiomethyl
PMP	*p*-methoxyphenyl
TADDOL	*2,22*,2-dimethyl-α,α′,α,α′-tetraphenyldioxolane-4,5-dimethanol
TBDPS	*tert*-butyldiphenylsilyl
xs	excess

TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)				Refs.
C_{3-11}			R^1	R^2		
	EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, –78 to >0°		Me	Me	(74)	
			Et	Me	(82)	1, 13
			n-Pr	Me	(90)	
			i-Pr	Me	(88)	
			n-Bu	Me	(89)	
			n-C_5H_{11}	Me	(93)	
			Ph	Et	(93)	
			n-C_7H_{15}	Me	(91)	
			n-C_9H_{19}	Me	(98)	
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.04–0.1 eq), Et$_2$O, 18–20°		R^1	R^2		
			Me	Et	(84)	2, 36
			Me	Me	(76)	
			Et	Me	(87)	
			Pr	Me	(91)	
			i-Pr	Me	(88)	
			n-Bu	Me	(90)	
			n-C_5H_{11}	Me	(94)	
			c-C_6H_{11}	Me	(85)	
			Ph	Et	(64)	
			n-C_7H_{15}	Me	(94)	
			n-C_9H_{19}	Me	(97)	
C_4 	EtMgBr (2–3 eq), Ti(O*i*-Pr)$_4$ (0.1–0.2 eq), THF, Et$_2$O, 15–20°	 (70)				47, 52
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, Et$_2$O, 15–20°	 (70–80)				47

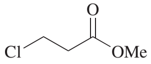
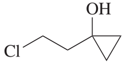
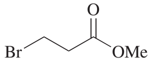
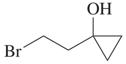
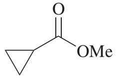
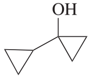
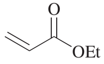
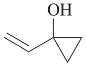
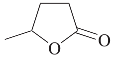
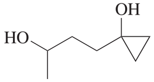
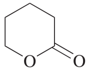
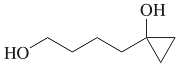
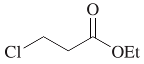
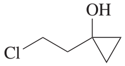
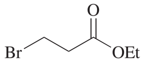
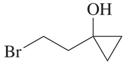
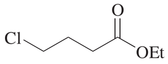
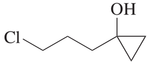
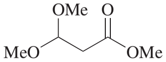
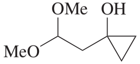
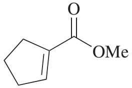
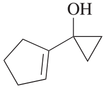
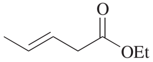
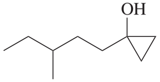
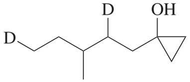
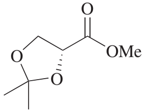
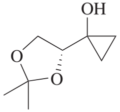
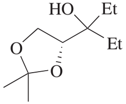
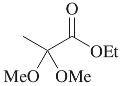
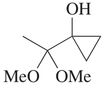
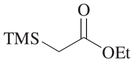
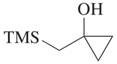
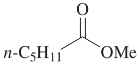
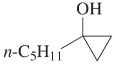
		EtMgBr (2.1 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et$_2$O, 0–20°		(>80)	50
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et$_2$O, 18–20°		(92)	50, 320
C$_5$					
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 20°		(99)	211
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt		(11)	37
		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, Et$_2$O, 15–20°		(70–80)	47
		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, Et$_2$O, 15–20°		(70–80)	47
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et$_2$O, rt		(93)	50, 185, 321
		EtMgBr (*x* eq), Ti(O*i*-Pr)$_4$ (*y* eq), Solvent, rt		*x* *y* Solvent 2 0.5 THF (86) 2.2 0.1 Et$_2$O (84)	 322 323
C$_6$					
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et$_2$O, rt		(85)	142

TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES (*Continued*)

	Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 0–20°	 (96)	324
C_7		EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, 5–10°	 (86)	38, 325
		EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (1.7 eq), Et$_2$O, rt	 (88)	41
		EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (1.7 eq), Et$_2$O, rt; then DCl, D$_2$O	 (86)	41
		EtMgBr (5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF/benzene, rt	 (60) +  (25)	323
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt	 (0)	37
		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt	 (67)	44
		EtMgBr (1.5 eq), MeMgBr (3 eq) , Ti(O*i*-Pr)$_4$ (1.5 eq), Et$_2$O, –78 to 0°	 (91)	71

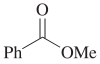
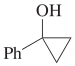
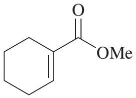
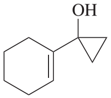
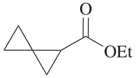
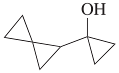
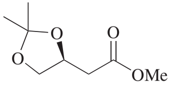
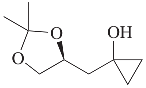
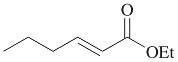
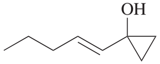
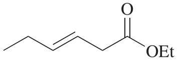
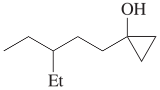
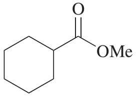
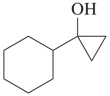
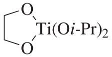
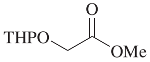
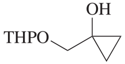
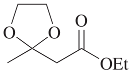
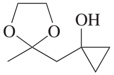
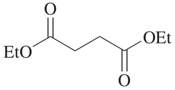
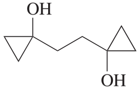
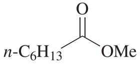
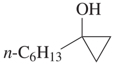
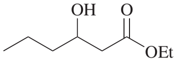
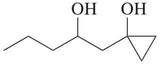
C_8		EtMgCl (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, –78°	 **I** (90–95)	326
		EtMgCl (2 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, –78°	**I** (34)	326
		1. EtMgCl (2 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, –78° 2. CH$_2$=CH$_2$, rt	**I** (60–75)	326
		1. EtMgCl (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, –78° 2. MeCH=CH$_2$, rt	**I** (55)	326
		EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, 5–10°	 (95)	325, 38, 201
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 20°	 (97)	211
		EtMgBr, Ti(O*i*-Pr)$_4$	 (80)	327
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, THF, rt	 (26)	37
		EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (1.7 eq), Et$_2$O, rt	 (85)	41

TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	EtMgBr (excess), $Ti(OY)_4$ (1.1 eq), THF, rt	 $Ti(OY)_4$ $Ti(Oi\text{-}Pr)_4$ (81) $ClTi(Oi\text{-}Pr)_3$ (76) $MeTi(Oi\text{-}Pr)_3$ (79)  (87) $Ti(OPh)_4$ (82) $Ti(OPMP)_4$ (93) $Ti(OCH_2CF_3)_4$ (68) $Ti[OCH(CF_3)_2]_4$ (82) $Ti(OTBS)_4$ (86)	72
	EtMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), THF, 15–20°	 (60)	47
	EtMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), THF, Et_2O, 15–20°	 (80)	305
	EtMgBr (2.4 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, 18–20°	 (80)	328
	EtMgBr (3 eq), $Ti(Oi\text{-}Pr)_4$ (0.1 eq), Et_2O, rt	 (95)	329
	EtMgBr (4 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF/Et_2O (4:1)	 (51)	52

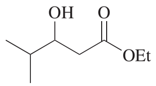
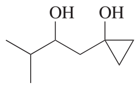
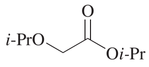
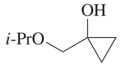
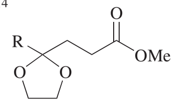
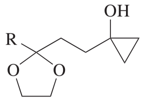
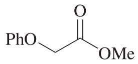
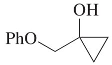
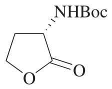
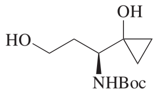
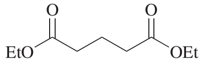
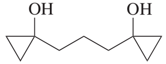
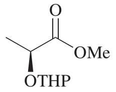
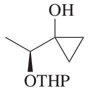
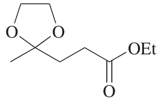
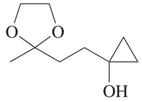
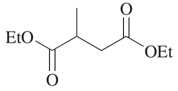
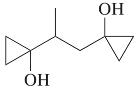
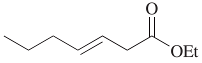
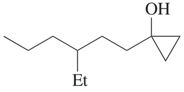
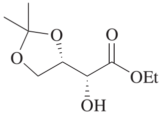
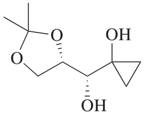
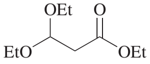
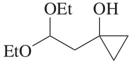
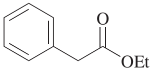
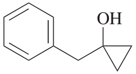
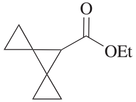
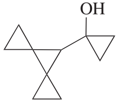
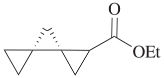
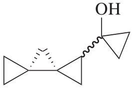
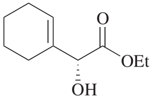
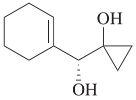
		EtMgBr (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF/Et$_2$O (4:1)		(51)	52
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.14 eq), Et$_2$O, 18–20°		(50)	46
C$_{8-14}$		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), THF, Et$_2$O, 18–20°		R Me (>84) 4-MeC$_6$H$_4$ (>78)	328
C$_9$		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.14 eq), Et$_2$O, 18–20°		(30)	46
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.3 eq), THF, 15–20°		(70)	47
		EtMgBr (5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, 18–20°		(90)	43
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, 15–20°		(70)	47
		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), THF, Et$_2$O, rt		(>80)	49
		EtMgBr (5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, Et$_2$O, 18–20°		(68)	43

TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	EtMgBr (6 eq), $Ti(Oi\text{-}Pr)_4$ (1.7 eq), Et_2O, rt	 (87)	41
	EtMgBr (4 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, rt	 (41)	193
	EtMgBr (2.5–3.0 eq), $Ti(Oi\text{-}Pr)_4$ (0.1–0.2 eq), THF, Et_2O, rt	 (99)	324, 49
C_{10}			
	EtMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), THF, 0–20°	 (84)	324
	EtMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, 20°	 (99)	211
 dr 3:2	EtMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, 20°	 (94) dr 3:2	211
	EtMgBr (5 eq), $ClTi(Oi\text{-}Pr)_3$ (2 eq), toluene, Et_2O, rt	 (43)	193, 330

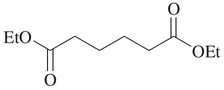
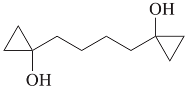
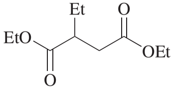
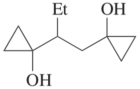
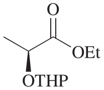
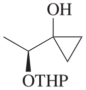
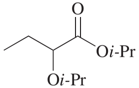
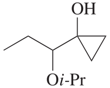
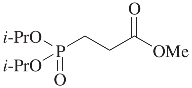
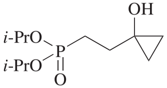
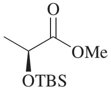
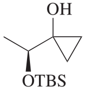
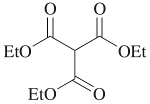
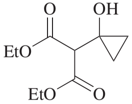
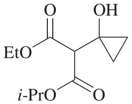
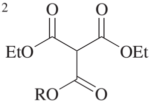
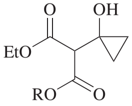
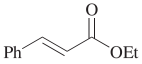
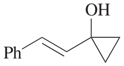
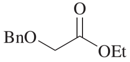
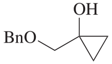
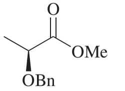
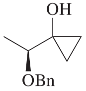
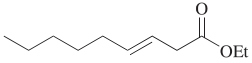
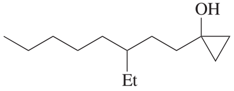
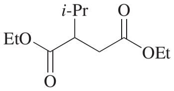
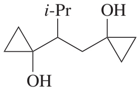
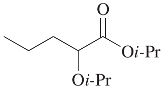
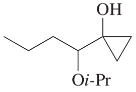
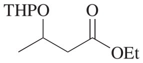
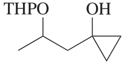
	EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, 18–20°	 (90)	43
	EtMgBr (5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, Et$_2$O, 18–20°	 (64)	43
	EtMgBr (3.0 eq), Ti(O*i*-Pr)$_4$ (0.25 eq), THF, Et$_2$O, 10–15°	 (79)	331
	EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.14 eq), Et$_2$O, 18–20°	 (55)	46
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, 0° to rt	 (67)	48
	EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, 15–20°	 (0)	47
	EtMgBr (8 eq), Ti(OEt)$_4$ (2 eq), THF, –40°	 **I** (45)	42
	EtMgBr (12 eq), Ti(O*i*-Pr)$_4$ (2 eq), LiO*i*-Pr (1 eq), THF, –40°	**I** (50) +  (1.3)	42

TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES (*Continued*)

	Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{10-12}		EtMgBr (6–7 eq), Ti(O*i*-Pr)$_4$ (0.3 eq), THF, 5°		R Et (19) *i*-Pr (1.3) *t*-Bu (3)	42
C_{11}		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, rt		(25)	37
		EtMgBr (4.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O/PhH, rt		(78)	332
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, 15–20°		(0)	47
		EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (1.7 eq), Et$_2$O, rt		(87)	41
		EtMgBr (5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, Et$_2$O, 18–20°		(85)	43
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.14 eq), Et$_2$O, 18–20°		(67)	46
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.25 eq), THF, Et$_2$O, PhH, rt		(88)	185

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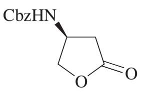
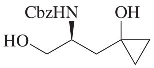
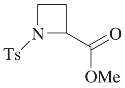
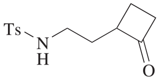
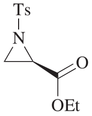
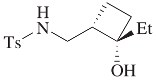
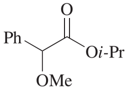
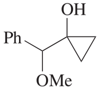
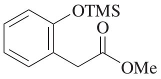
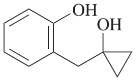
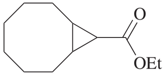
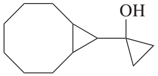
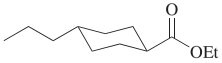
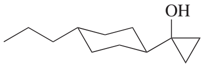
<tr><td>C₁₂</td><td></td><td>EtMgBr (3 eq),
Ti(O<i>i</i>-Pr)₄ (0.4 eq),
THF, 15–20°</td><td></td><td>(70)</td><td>47</td></tr>
<tr><td></td><td></td><td>1. EtMgBr,
ClTi(O<i>i</i>-Pr)₃, THF, 20°
2. CaSO₄</td><td></td><td>(70)</td><td>333</td></tr>
<tr><td></td><td></td><td>EtMgBr (<i>x</i> eq),
YTi(OR)₃,
THF, 20°</td><td></td><td><table>
<tr><th>R</th><th>Y</th><th>mol %</th><th><i>x</i></th><th></th></tr>
<tr><td><i>i</i>-Pr</td><td>Cl</td><td>50</td><td>1</td><td>(0)</td></tr>
<tr><td><i>i</i>-Pr</td><td>Cl</td><td>75</td><td>2</td><td>(0)</td></tr>
<tr><td><i>i</i>-Pr</td><td>Cl</td><td>100</td><td>3</td><td>(14)</td></tr>
<tr><td><i>i</i>-Pr</td><td>Cl</td><td>50</td><td>4</td><td>(36)</td></tr>
<tr><td><i>i</i>-Pr</td><td>Cl</td><td>75</td><td>4</td><td>(40)</td></tr>
<tr><td><i>i</i>-Pr</td><td>Cl</td><td>100</td><td>4</td><td>(52)</td></tr>
<tr><td><i>i</i>-Pr</td><td>Cl</td><td>150</td><td>4</td><td>(50)</td></tr>
<tr><td><i>i</i>-Pr</td><td>O<i>i</i>-Pr</td><td>50</td><td>4</td><td>(32)</td></tr>
<tr><td><i>i</i>-Pr</td><td>O<i>i</i>-Pr</td><td>75</td><td>4</td><td>(45)</td></tr>
<tr><td><i>i</i>-Pr</td><td>O<i>i</i>-Pr</td><td>100</td><td>4</td><td>(47)</td></tr>
<tr><td>Et</td><td>OEt</td><td>100</td><td>4</td><td>(23)</td></tr>
</table></td><td>333</td></tr>
<tr><td></td><td></td><td>EtMgBr (3 eq),
Ti(O<i>i</i>-Pr)₄ (0.14 eq),
Et₂O, 18–20°</td><td></td><td>(55)</td><td>46</td></tr>
<tr><td></td><td></td><td>EtMgBr,
Ti(O<i>i</i>-Pr)₄ ,
Et₂O, THF, 20°</td><td></td><td>(85)</td><td>334</td></tr>
<tr><td></td><td></td><td>EtMgBr (2 eq),
Ti(O<i>i</i>-Pr)₄ (0.2 eq),
Et₂O, 15–20°</td><td></td><td>(84)</td><td>335</td></tr>
<tr><td></td><td></td><td>EtMgBr (2.5 eq),
Ti(O<i>i</i>-Pr)₄ (0.2 eq),
Et₂O, rt</td><td></td><td>(95)</td><td>336</td></tr>
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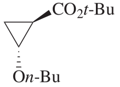
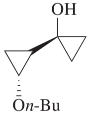
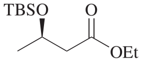
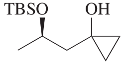
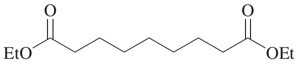
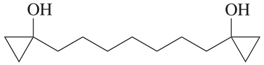
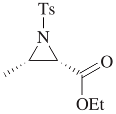
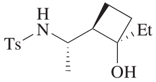
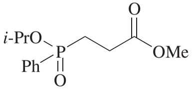
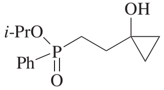
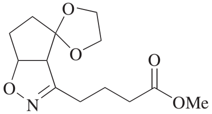
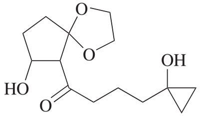
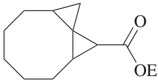
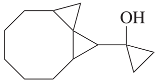
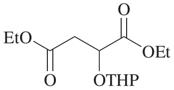
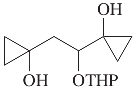
TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{12}$			
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 20°	 (52)	211
	EtMgBr (excess), Ti(O*i*-Pr)$_4$, rt	 (87)	337
C$_{13}$			
	EtMgBr (5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, 18–20°	 (85)	43
	EtMgBr (4 eq), ClTi(O*i*-Pr)$_3$, THF, 20°	 (38)	333
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, 0°	 (37)	48
	EtMgBr (10 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, THF, –78°	 (12)	51
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 15–20°	 (81)	335
	EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (0.5 eq), Et$_2$O, rt	 (75)	338

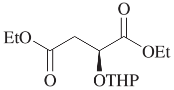
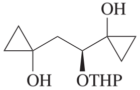
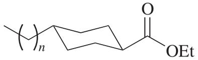
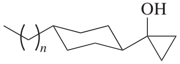
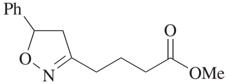
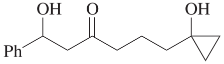
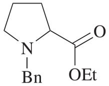
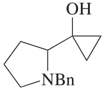
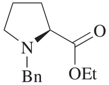
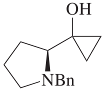
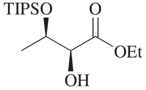
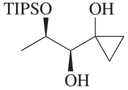
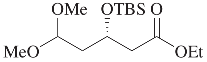
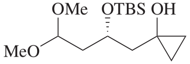
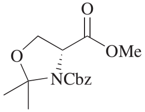
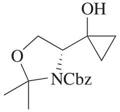
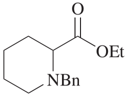
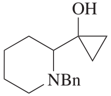
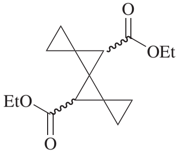
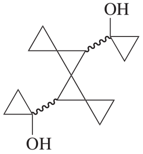
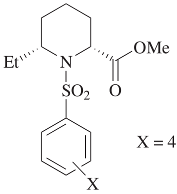
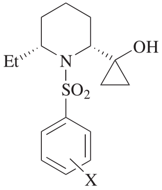
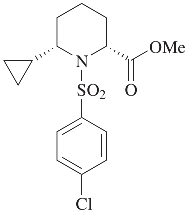
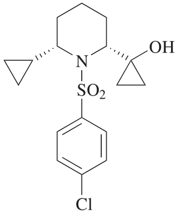
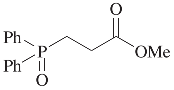
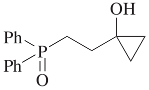
		EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (0.5 eq), Et$_2$O, rt		(>50)	339
C$_{13–14}$		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt		*n* 3 (95) 4 (95)	340, 341, 336
C$_{14}$		EtMgBr (10 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, THF, –78°		(40)	51
		EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (0.25 eq), THF, reflux		(45)	45
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt		(92)	342
C$_{15}$		EtMgBr (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt		(56)	193
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), or ClTi(O*i*-Pr)$_3$ (0.2 eq), THF, rt		(77)	153
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.5 eq), Et$_2$O, rt		(64)	343
		EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 18–20°		(60)	45

TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 18–20°	 (98)	211
 X = 4-F, 4-Cl, 3,4-F$_2$	EtMgBr, Ti(O*i*-Pr)$_4$	 (—)	344
C_{16} 	EtMgBr, Ti(O*i*-Pr)$_4$	 (—)	344
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, 0°	 (64)	48

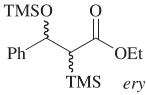
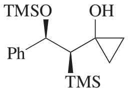
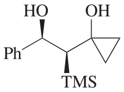
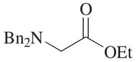
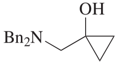
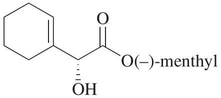
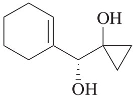
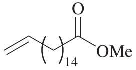
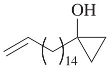
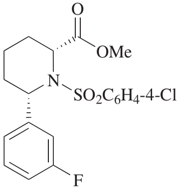
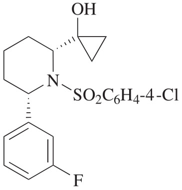
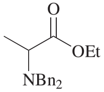
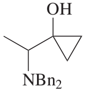
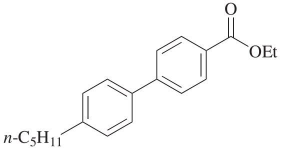
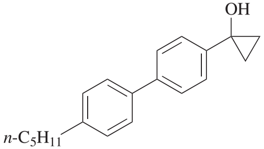
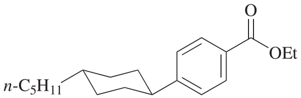
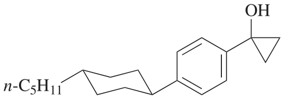
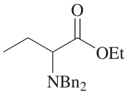
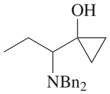
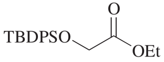
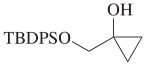
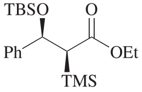
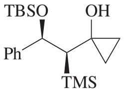
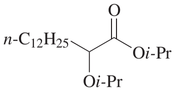
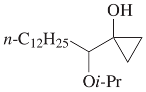
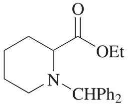
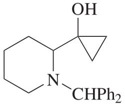
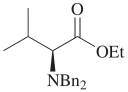
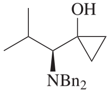
C_{17}	 *erythro*/*threo* = 1:1	EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, rt	 (52) +  (5–10)	44
C_{18}		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, 18–20°	 (90)	45
		EtMgBr (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (43)	193, 330
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et_2O, rt	 (>86)	39
C_{19}		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.3 eq), THF, 0°	 (72)	345
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, 18–20°	 (90)	45
C_{20}		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, rt	 (high)	336

TABLE 1. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM ETHYL GRIGNARD REAGENT AND TITANIUM ALKOXIDES (*Continued*)

	Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt	 (high)	336
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 18–20°	 (85)	45
		EtMgBr (2.4 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, Et$_2$O, –10 to –5°	 (80)	346
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, THF, rt	 (60)	44
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.14 eq), Et$_2$O, 18–20°	 (69)	46
C_{21}		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 18–20°	 (77)	347
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 18–20°	 (92)	45

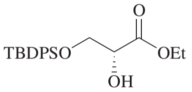
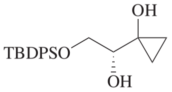
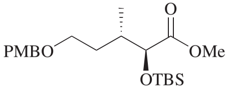
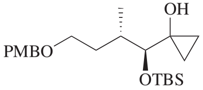
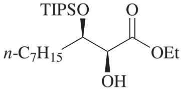
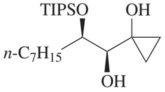
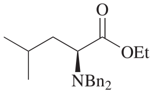
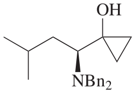
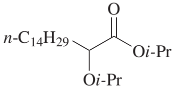
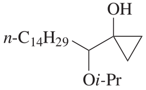
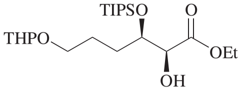
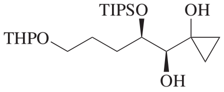
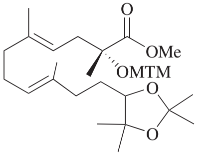
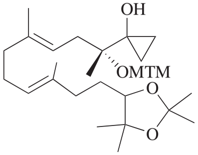
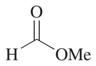
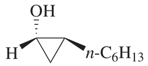
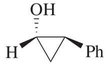
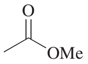
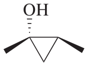
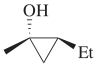
		EtMgBr (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (62)	193
		EtMgBr (excess), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, rt	 (99)	348
		EtMgBr (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (43)	193
C$_{22}$		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 18–20°	 (95)	45
		EtMgBr (3 eq), Ti(O*i*-Pr)$_4$ (0.14 eq), Et$_2$O, 18–20°	 (70)	46
		EtMgBr (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (49)	193
C$_{24}$		EtMgBr (5 eq), ClTi(O*i*-Pr)$_3$ (2.5 eq), THF, 0° to rt	 (60)	194

TABLE 2. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM OTHER GRIGNARD REAGENTS AND TITANIUM ALKOXIDES

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 	*n*-$C_8H_{17}MgBr$ (2 eq), $ClTi(Oi\text{-}Pr)_3$ (0.1 eq), THF, 18–20°	 (72)	70
	$PhCH_2CH_2MgBr$ (2 eq), $ClTi(Oi\text{-}Pr)_3$ (0.1 eq), THF, 18–20°	 (60)	70
C_3 	*n*-PrMgBr (3 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, –78°	 **I** (67)	13
	n-PrMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (0.04-0.1 eq), Et_2O, 20°	**I** (57)	36
	n-PrBr (2 eq), Mg (4 eq), $ClTi(Oi\text{-}Pr)_3$ (0.1 eq), THF, 18–20°	**I** (80)	70
	n-BuMgBr (3 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, –78 to 0°	 (78) **I**	13
	n-BuMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (0.04–0.1 eq), Et_2O, 20°	**I** (73)	36
	n-$C_6H_{13}MgBr$ (1–2 eq), MeMgI (1–2 eq), $Ti(Oi\text{-}Pr)_4$ (0.15–1 eq), Et_2O, rt	 (70–82) dr 24:1	34

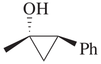
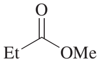
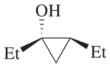
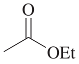
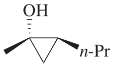
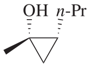
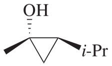
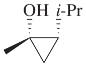
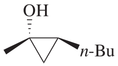
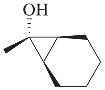
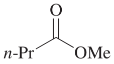
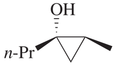
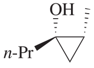
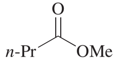
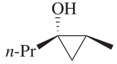
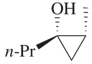
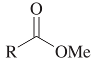
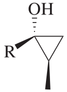
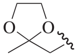
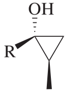
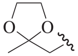
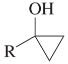
	$PhCH_2CH_2MgBr$ (2 eq), $ClTi(O\textit{i}\text{-}Pr)_3$ (0.1 eq), THF, 18–20°	 (83)	70
C_4 	*n*-BuMgBr (3 eq), $Ti(O\textit{i}\text{-}Pr)_4$ (1 eq), Et_2O, –78 to 0°	 **I** (74)	13
	n-BuMgBr (2 eq), $Ti(O\textit{i}\text{-}Pr)_4$ (0.04–0.1 eq), Et_2O, 20°	**I** (74)	36
	*n*-$C_5H_{11}MgBr$ (2.2 eq), $Ti(O\textit{i}\text{-}Pr)_4$ (0.15 eq), Et_2O or THF, rt	 +  (75) dr 20:1	33
	i-$C_5H_{11}MgBr$ (3 eq), $Ti(O\textit{i}\text{-}Pr)_4$ (1 eq), Et_2O, rt	 +  (67) dr 23:1	33
	n-$C_6H_{13}MgBr$ (2.2 eq), $Ti(O\textit{i}\text{-}Pr)_4$ (1 eq), THF, –78° to rt	 **I** (75)	62
	n-$C_6H_{13}MgBr$ (1.1 eq), $MeTi(O\textit{i}\text{-}Pr)_3$ (1 eq), THF, –78° to rt	**I** (84)	62
	c-$C_6H_{11}MgBr$ (2.2 eq), $Ti(O\textit{i}\text{-}Pr)_4$ (0.1 eq), THF, rt	 (41)	62
C_5 	*n*-PrMgBr (2.2 eq), $Ti(O\textit{i}\text{-}Pr)_4$ (0.15 eq), Et_2O or THF, rt	 **I** +  **II** Solvent dr Et_2O (76) 5.5:1 THF (84) 14:1	33

TABLE 2. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM OTHER GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	n-PrMgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt	 **I** +  **II** (71) dr 10:1	33
	i-PrMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.15 eq), Et_2O or THF, rt	**I** + **II** Solvent — dr Et_2O (70) 4:1 THF (73) 10:1	33
	i-PrMgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt	**I** + **II** (68) dr 10: 1	33
C_{5-8} 	MeMgI (1.5 eq), *n*-PrMgBr (1.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et_2O or THF, 0°	 R — *cis*/*trans* *n*-Pr (65–67) — *t*-Bu (55) 40:60 $Cl(CH_2)_3$ (73–74) — *n*-C_5H_{11} (75) —  (80) —	34
	MgMgI (1.5 eq), *n*-PrMgBr (1.5 eq), Ti(O*i*-Pr)$_4$ (0.15 eq), THF, rt	 R — *cis*/*trans* *n*-Pr (68) — *t*-Bu (49) 25:75 $Cl(CH_2)_3$ (67) — *n*-C_5H_{11} (71) —  (80) 95:5	34
R = *n*-Pr, *n*-Bu, *n*-C_5H_{11}	$BrMg(CH_2)_4MgBr$ (1 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et_2O, –10 to 15°	 (35–43)	54

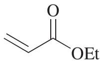
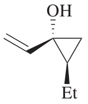
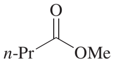
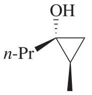
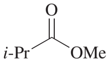
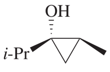
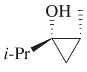
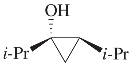
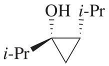
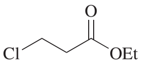
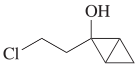
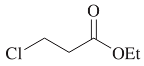
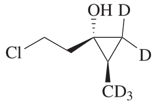
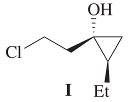
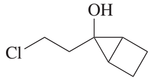
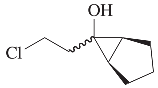
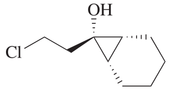
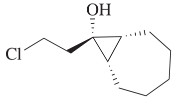
C_5 	n-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt		(0)	37
	MeMgI (*x* eq), *n*-PrMgBr (*y* eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, rt	 **I**	*x* *y* **I** 1 1 (35–56) 2 1 (47–60) 1 2 (77) 2 2 (85) 1.5 2 (88) 1.5 1.5 (88–91)	34
	n-PrMgBr (3 eq), Ti(OPr-*i*)$_4$ (0.2–1 eq), Et$_2$O or THF, rt	**I** (73–84) dr >4:1		34
	*n*-PrMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.15 eq), Et$_2$O or THF, rt	 **I** +  **II**	Solvent dr Et$_2$O (67) 1:1 THF (58) 2:1	33
	i-PrMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.15 eq), Et$_2$O or THF, rt	**I + II**	Solvent dr Et$_2$O (67) 1:1 THF (60) 2:1	33
	n-PrMgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt	**I + II** (50) dr 2:1		33
	i-C$_5$H$_{11}$MgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt	 + 	(45) dr 4:1	33
	*c*-C$_3$H$_5$MgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O/THF (2:3), rt		(0)	63

TABLE 2. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM OTHER GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	$(CD_3)_2CHMgBr$ (2 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, rt	 (46)	17
	n-BuMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O or THF, rt	 **I** (65)	37, 322
	n-BuMgBr (2.5 eq), $Ti(TADDOL)_2$ (0.2 eq), Et_2O, rt	**I** (66) 52% ee	37
	n-BuMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), (*S*)-$HO(CH_2)_2CH(OH)Me$ (0.2 eq), Et_2O, rt	**I** (44) 6% ee	37
	c-C_4H_7MgBr (4 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), THF	 (46)	63
	c-C_5H_9MgCl (3 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, THF	 (63) *exo*/*endo* = 63:37	63
	c-$C_6H_{11}MgBr$ (4 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, THF, rt	 (17)	63
	c-$C_7H_{13}MgBr$ (4 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, THF	 (56)	63

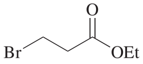
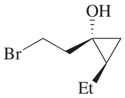
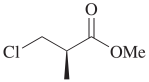
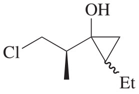
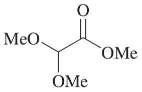
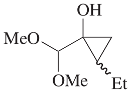
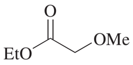
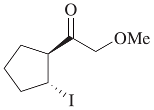
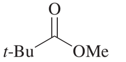
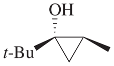
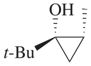
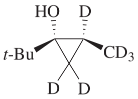
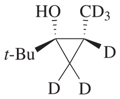
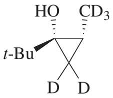
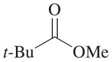
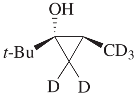
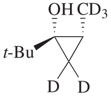
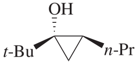
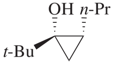
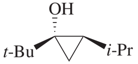
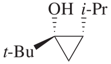
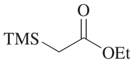
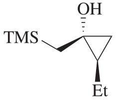
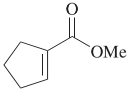
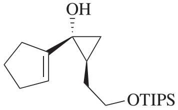
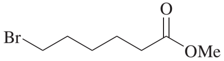
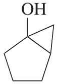
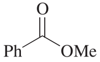
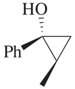
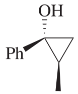
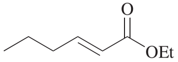
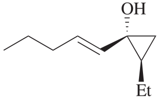
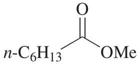
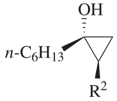
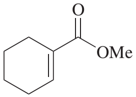
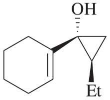
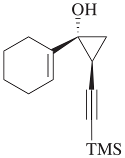
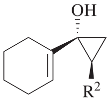
		*n*-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF or Et$_2$O, rt		(48)	37, 322
		*n*-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt		(24) 1:1 dr	37
		*n*-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$		(0)	349
		*c*-C_5H_9MgCl (3 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –78 to –30°; then I_2		(16)	90
C_6		*n*-PrMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.15 eq), Et$_2$O or THF, rt	 **I** +  **II**	Solvent (dr) Et$_2$O (49) 1:3 THF (45) 1:3	33
		i-PrMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.15 eq), THF, rt	**I + II** (53) dr 1:3		33
		i-PrMgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O or THF, rt	**I + II**	Solvent, **I + II**, dr Et$_2$O (54) 1:1.6 THF (44) 1:1	33
		i-C_3D_7MgBr (3 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, rt	 + 	(55) dr 1:1.4	33
		$(CD_3)_2$CHMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.15 eq), Et$_2$O, rt		(51) dr 7:3	34

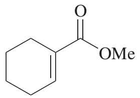
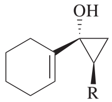
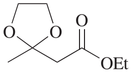
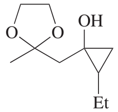
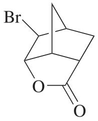
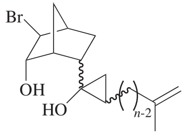
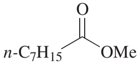
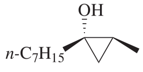
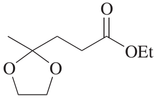
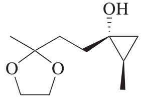
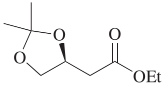
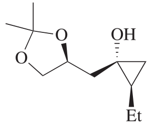
TABLE 2. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM OTHER GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$(CD_3)_2CHMgBr$ (3 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, rt	 +  (50) dr 1:1.2	33
	n-$C_5H_{11}MgBr$ (3 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, rt	 +  (48) dr 1:1.2	33
	i-$C_5H_{11}MgBr$ (3 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, rt	 +  (37) dr 3:1	33
C_7 	n-BuMgBr (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (0.1 eq), Et_2O, rt	 (56)	44
	$TIPSO(CH_2)_4MgCl$ (4 eq), $ClTi(Oi\text{-}Pr)_3$ (0.1 eq), THF, 20°	 (60)	201
	Mg (2 eq), $MeTi(Oi\text{-}Pr)_3$ (1 eq), THF, rt	 (16)	62
C_8 	i-PrMgCl (2.0 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, –78°	 **I** (0)	326
	i-PrMgBr (3.2 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, rt	**I** (48)	326

	i-PrMgCl (3.2 eq), Ti(Oi-Pr)$_4$ (1 eq), Et$_2$O, rt; then MeCH=CH$_2$	 (45)	326
	n-BuMgBr (2.5 eq), Ti(Oi-Pr)$_4$ (0.2 eq), Et$_2$O, rt	 (15)	37
	R^{1}Br (2 eq), Mg (4 eq), ClTi(Oi-Pr)$_3$ (0.1 eq), THF, 18–20°	 R^1 — R^2 n-Bu — Et — (81) n-C$_8$H$_{17}$ — n-C$_6$H$_{13}$ — (88)	70
	n-BuMgBr (2 eq), Ti(Oi-Pr)$_4$ (0.1 eq), Et$_2$O, 20°	 (46–54)	201
	TMSC≡C(CH$_2$)$_2$MgBr (2 eq), Ti(Oi-Pr)$_4$ (0.1 eq), Et$_2$O, 20°	 (0)	201
	R^{1}MgBr (x eq), ClTi(Oi-Pr)$_3$ (y eq), THF	 (0)	201

R^1	x	y	R^2	Temp (°)
CH$_2$=CH(CH$_2$)$_2$	2	0.1	CH$_2$=CH	20
2-furyl(CH$_2$)$_2$	3	1	2-furyl	0 to rt
Ph(CH$_2$)$_2$	xs	0.5	Ph	18–20

TABLE 2. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM OTHER GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	$R(CH_2)_2MgCl$ (4 eq), $ClTi(Oi\text{-}Pr)_3$ (0.1 eq), THF, 20°	 R $THPO(CH_2)_2$ (46) $TIPSO(CH_2)_2$ (77)	201
	*n*-BuMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, rt	 (0)	37
	$CH_2{=}C(Me)(CH_2)_nMgBr$ (3 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt	 *n* 3 (57) 4 (51)	350
C_9 	*n*-PrMgBr (3.2 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, –78°	 **I** (94)	13
	n-PrMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (0.04–0.1 eq), Et_2O, 20°	**I** (90)	36
	*n*-PrMgBr (4 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O/THF (2:3), rt	 (80)	351
	*n*-BuMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, rt	 (80) dr 4:4:2	37

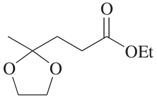
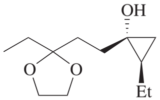
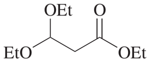
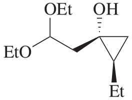
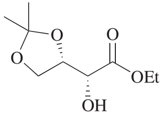
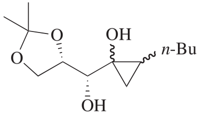
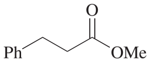
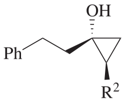
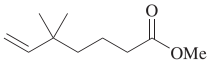
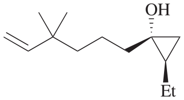
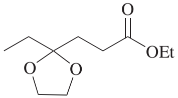
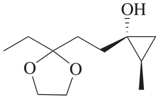
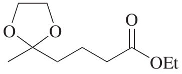
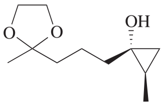
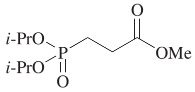
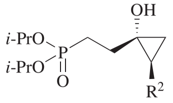
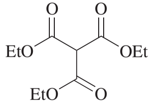
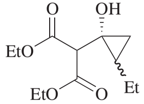
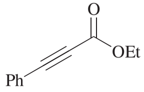
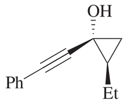
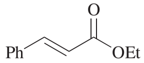
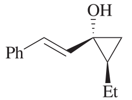
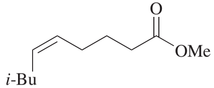
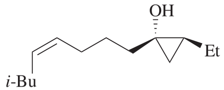
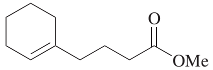
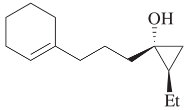
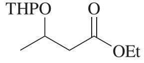
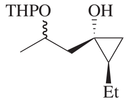
		*n*-BuMgBr (4 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O/THF (3:2), rt		(90) dr >94: 6	351
		*n*-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.1–0.2 eq), Et$_2$O, rt		(92)	37
		*n*-C$_6$H$_{13}$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), THF, rt		(57) dr 1:0.7:0.3:0.25	193
C$_{10}$		R^{1}Br (2 eq), Mg (4 eq), ClTi(O*i*-Pr)$_3$ (0.1 eq), THF, 18–20°		R^1 R^2 *n*-Pr Me (83) *n*-Bu Et (79)	70
		*n*-BuMgBr (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et$_2$O, rt		(61)	55
		*n*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, THF, rt		(78) dr >94:6	351
		*n*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), THF, rt		(78)	352

TABLE 2. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM OTHER GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	R^1MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, 0° to rt	 R^1 R^2 *n*-Pr Me (60) *n*-Bu Et (71)	48
	*n*-BuMgBr (*x* eq), Ti(OR)$_4$ (*y* eq), THF	 *x* R *y* Temp (°) 8 Et 2 –40 (15) 6–7 *i*-Pr 0.3 5 (7)	42
C_{11} 	*n*-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, rt	 (15)	37
	*n*-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, rt	 (0)	37
	*n*-BuMgBr (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et_2O, rt	 (45)	55
	*n*-BuMgBr (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et_2O, rt	 (91)	55
	*n*-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, rt	 (65) dr 1:1	37, 349

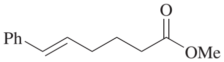
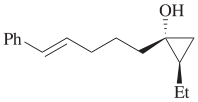
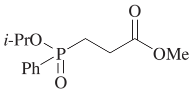
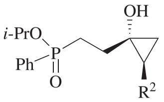
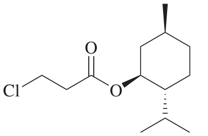
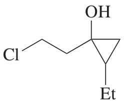
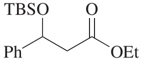
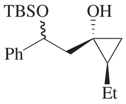
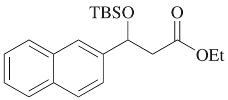
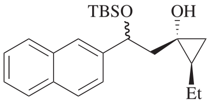
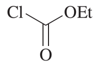
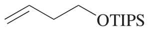
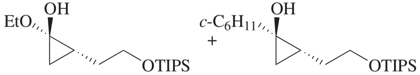
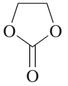
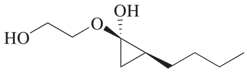
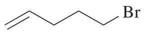
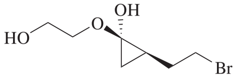
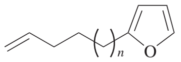
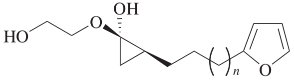
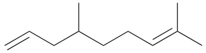
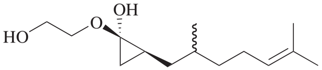
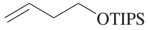
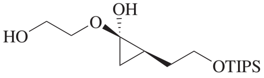
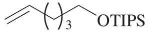
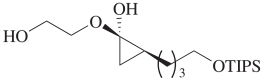
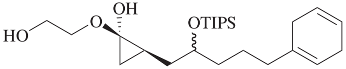
C_{13}		n-BuMgBr (5 eq), ClTi(Oi-Pr)$_3$ (0.5 eq), Et_2O, rt		(40)	55
		R^{1}MgBr (2.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, 0°		R^1 R^2 n-Pr Me (40) n-Bu Et (41)	48
		n-BuMgBr (2.5 eq), Ti(Oi-Pr)$_4$ (0.2 eq), Et_2O, rt		(0)	37
C_{17}		n-BuMgBr (2.5 eq), Ti(Oi-Pr)$_4$ (0.2 eq), Et_2O, rt		(54)	37, 349
C_{21}		n-BuMgBr (2.5 eq), Ti(Oi-Pr)$_4$ (0.2 eq), Et_2O, rt		(60)	37

TABLE 3. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE

Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		c-C_6H_{11}MgCl (5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, –5°	 (37) + (25)	85
		c-C_6H_{11}MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, 0°	 (47) dr 4:1–5:1	85
		c-C_6H_{11}MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, 0°	 (58) dr 2:1	86
		c-C_6H_{11}MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, 0°	 n dr 1 (43) 2:1 2 (49) 2:1	86
		c-C_6H_{11}MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, 0°	 (53) dr 4:1–5:1	85
		c-C_6H_{11}MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF	 Temp (°) 20 (17) 0 (47) –10 (43) –35 (5)	85
		c-C_5H_9MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, 0°	 (41) dr 4:1–5:1	85
		c-C_5H_9MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, 0°	 (37) dr 4:1–5:1	85

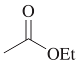
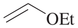
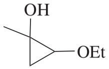
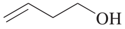
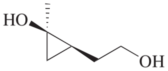
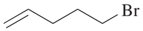
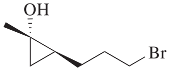
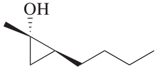
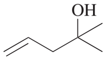
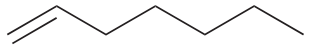
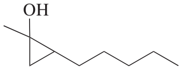
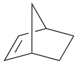
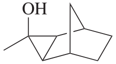
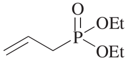
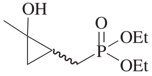
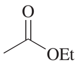
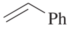
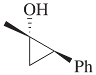
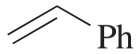
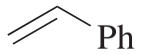
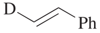
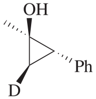
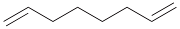
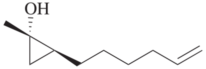
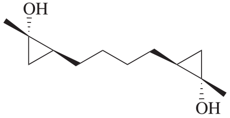
C_4 		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.05 eq), Et$_2$O, reflux		(0)	53
		EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, reflux		(42)	64
		*c*-C$_6$H$_{11}$MgCl (4.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt		(64)	60
		*c*-C$_6$H$_{11}$MgCl (4.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt		(95)	60
		EtMgBr (4 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, reflux		(56)	64
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.05 eq), Et$_2$O, reflux		(0)	53
		*c*-C$_6$H$_{11}$MgCl (4.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt		(37)	60
		*c*-C$_6$H$_{11}$MgCl, Ti(O*i*-Pr)$_4$		(54) dr 1:3	48

TABLE 3. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	 *x* eq	EtMgBr (*y* eq), $Ti(Oi\text{-}Pr)_4$ (*z* eq), Et_2O, reflux	 **I** *x* *y* *z* 2 2 0.1 (36) 2 2.5 0.05 (42) 2 2.5 0.1 (54) 2 2.5 0.2 (55) 2 2.5 0.5 (53) 2 2.5 1.0 (41) 1 2.5 0.2 (35) 3 2.5 0.2 (53)	53, 353
		RMgX (2–4.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.05–1 eq), Et_2O, reflux	**I** R X *n*-Pr Br (71) *i*-Pr Br (32–72) *n*-Bu Br (78) *i*-Bu Br (27) *c*-C_6H_{11} Cl (30–53)	353
		$(CD_3)_2CHMgBr$ (3 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, reflux	**I** (68)	353
		EtMgBr (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (0.2 eq), Et_2O, reflux	 (29)	30
		*c*-C_6H_{11}MgCl (4.5 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), THF, rt	 (49) +  (10)	60

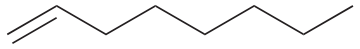
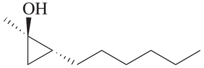
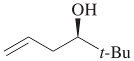
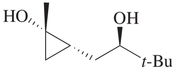
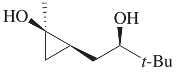
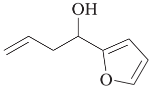
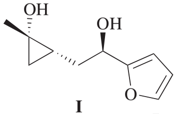
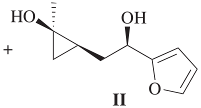
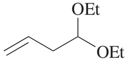
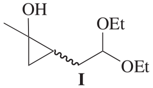
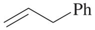
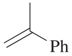
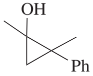
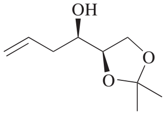
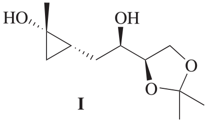
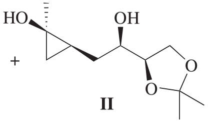
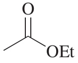
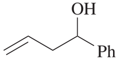
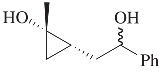
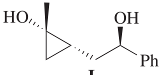
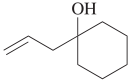
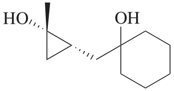
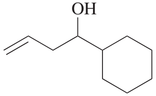
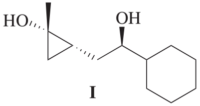
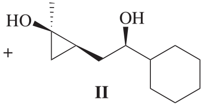
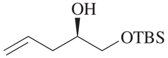
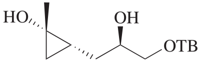
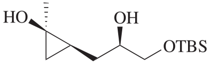
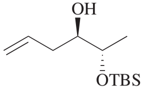
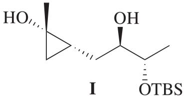
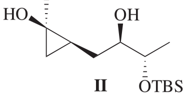
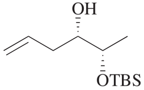
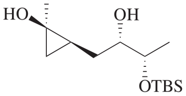
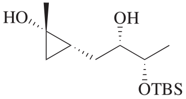
	c-$C_6H_{11}MgBr$ (6 eq), $Ti(Oi\text{-}Pr)_4$ (3 eq), PhMe, rt	 (>77)	354
	1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. c-C_5H_9MgCl (4.4 eq), THF, rt	 **I** +  **II** **I** + **II** (58) dr 8.3:1	74
	1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. c-C_5H_9MgCl (4.4 eq), THF, rt	 **I** +  **II** **I** + **II** (56) dr 5:1	74
	n-BuMgBr (3 eq), $Ti(Oi\text{-}Pr)_4$ (0.5 eq), Et_2O, reflux	 **I** (80)	66
	i-PrMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (0.5 eq), Et_2O, rt	**I** (54)	67
	c-C_5H_9MgCl (4 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF/hexane, rt	 (80)	318
	EtMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (0.05 eq), Et_2O, reflux	 (0)	53
	1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. c-C_5H_9MgCl (4 eq), THF, rt	 **I** +  **II** **I** + **II** (32) dr 5.6:1	74

TABLE 3. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		EtMgBr (4 eq), $Ti(Oi\text{-}Pr)_4$ (1eq), Et_2O, reflux	 (58)	64
		1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. $c\text{-}C_5H_9MgCl$ (4 eq), THF, rt	 **I** +  **II** **I** + **II** (68) dr 12.2:1	74
		EtMgBr (4 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, reflux	 (26)	64
		1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. $c\text{-}C_5H_9MgCl$ (4 eq), THF, rt	 **I** +  **II** **I** + **II** (65) dr 8.6:1	74
		1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. $c\text{-}C_5H_9MgCl$ (4 eq), THF, rt	 **I** +  **II** **I** + **II** (42) dr 4.2:1	74
		1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. $c\text{-}C_5H_9MgCl$ (4 eq), THF, rt	 **I** +  **II** **I** + **II** (60) dr 3.3:1	74
		1. $Ti(Oi\text{-}Pr)_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. $c\text{-}C_5H_9MgCl$ (4 eq), THF, rt	 **I** +  **II** **I** + **II** (56) dr 3.5:1	74

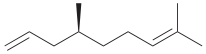
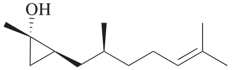
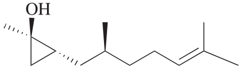
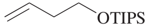
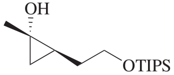
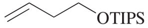
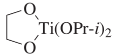
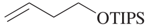
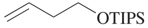
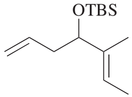
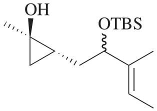
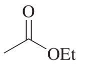
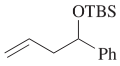
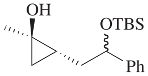
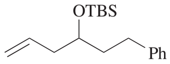
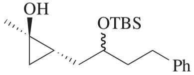
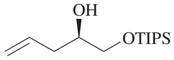
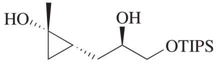
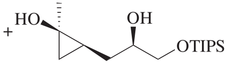
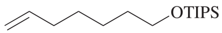
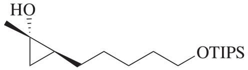
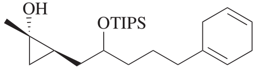
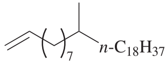
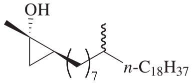
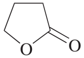
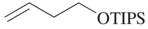
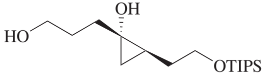
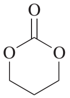
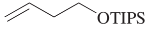
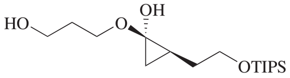
	c-$C_6H_{11}MgCl$ (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, rt	 **I** + **I** + **II** (87) dr 1:1  **II**	60
	c-$C_6H_{11}MgCl$ (4.5 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), THF, rt	 **I** (75)	60
	c-C_5H_9MgCl (excess), $Ti(OY)_4$ (1.1 eq), THF, rt	**I** $Ti(OY)_4$ $Ti(Oi\text{-}Pr)_4$ (71) $ClTi(Oi\text{-}Pr)_3$ (78) $MeTi(Oi\text{-}Pr)_3$ (84)  (61)	72
	c-C_5H_9MgCl (excess), $Ti(OY)_4$ (1.1 eq), THF, rt	**I** $Ti(OY)_4$ $Ti(OPh)_4$ (55) $Cl_2Ti(OPh)_2$ (38) $Ti(OPMP)_4$ (53) $Ti(OC_6H_3Me_2\text{-}2,6)_4$ (45) $Ti(OCH_2CF_3)_4$ (25) $Ti[OCH(CF_3)_2]_4$ (9) $Ti(OTBS)_4$ (53)	72
	c-$C_6H_{11}MgBr$ (6 eq), $Ti(Oi\text{-}Pr)_4$ (3 eq), PhMe, rt	**I** (>76)	354
	c-$C_6H_{11}MgBr$ (6 eq), $Ti(Oi\text{-}Pr)_4$ (3 eq), PhMe, rt	 (>52)	354

TABLE 3. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_4$ 		c-C_6H_{11}MgBr (6 eq), Ti(Oi-Pr)$_4$ (3 eq), PhMe, rt	 (>62)	354
		c-C_6H_{11}MgBr (6 eq), Ti(Oi-Pr)$_4$ (3 eq), PhMe, rt	 (>62)	354
		1. Ti(Oi-Pr)$_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. c-C_5H_9MgCl (4 eq), THF, rt	 **I** +  **II** **I** + **II** (56) dr 7.4:1	74
		c-C_6H_{11}MgCl (4.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, rt	 (71)	60
		c-C_6H_{11}MgCl (4.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, rt	 (42)	60
		c-C_6H_{11}MgCl (7.4 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, Et$_2$O, rt	 (64)	355
		c-C_6H_{11}MgCl (4.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, rt	 (33)	60
		c-C_5H_9MgCl (6 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, 0°	 (53)	85

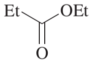
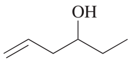
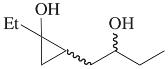
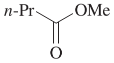
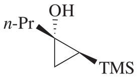
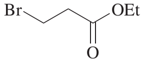
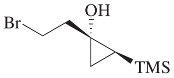
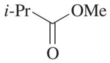
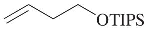
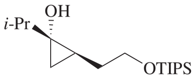
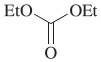
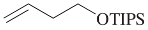
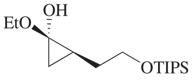
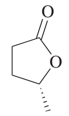
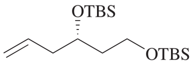
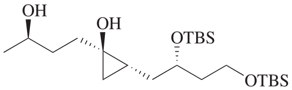
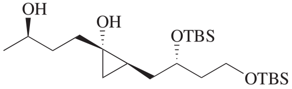
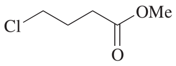
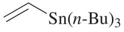
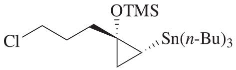
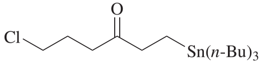
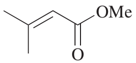
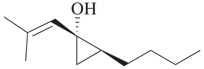
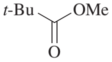
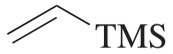
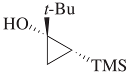
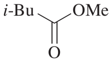
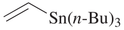
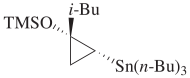
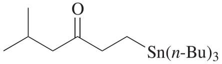
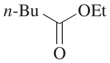
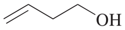
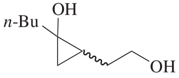
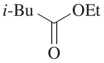
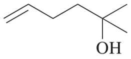
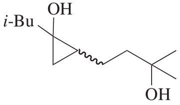
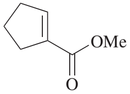
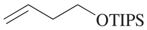
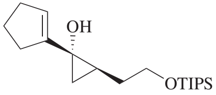
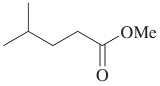
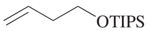
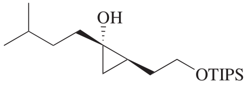
C_5			*i*-PrMgBr (4.0 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, rt	 (71)	356
			*i*-PrMgCl (2.9 eq), ClTi(O*i*-Pr)$_3$ (1.5 eq), Et$_2$O, –60°, then –25 to 0°	 (80) dr 87:13	69
			*i*-PrMgCl (2.9 eq), ClTi(O*i*-Pr)$_3$ (1.5 eq), Et$_2$O, –60° to rt	 (42) dr 77:23	69, 357
			*c*-C$_6$H$_{11}$MgCl (4.5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (62)	60
			*c*-C$_6$H$_{11}$MgCl (5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, –5°	 (25–30)	85
			*c*-C$_6$H$_{11}$MgBr (6 eq), Ti(O*i*-Pr)$_4$ (3 eq), PhMe, rt	 **I** +  **I** + **II** (92) dr 1:1 **II**	354
			1. *c*-C$_5$H$_9$MgCl (4–5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF 2. TMSOTf, pyr, CH$_2$Cl$_2$, 0° to rt	 (7) +  (24)	358

TABLE 3. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		c-$C_6H_{11}MgCl$ (4.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, rt	 (37)	60
		i-PrMgCl (2.9 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), Et$_2$O, –60 to –25°	 (82) dr 93:7	357
		1. c-C_5H_9MgCl (4-5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF 2. TMSCl	 (14) +  (30)	358
C_7				
		EtMgBr (4 eq), Ti(Oi-Pr)$_4$ (1 eq), Et$_2$O, reflux	 (37)	64
		RMgBr (5 eq), Ti(Oi-Pr)$_4$ (1 eq), Et$_2$O, reflux	 R Et (85) *i*-Pr (63) *n*-Bu (62) c-C_6H_{11} (33)	65
		c-C_5H_9MgCl (3.9 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF	 (53–77)	152
		c-$C_6H_{11}MgCl$ (4.5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (65)	60

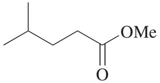
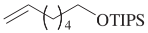
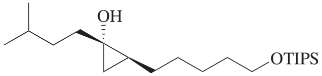
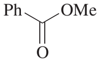
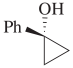
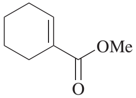
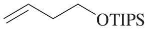
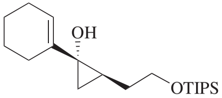
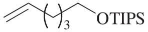
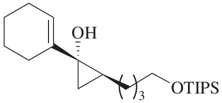
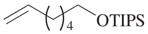
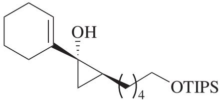
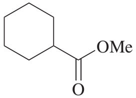
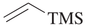
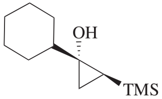
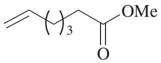
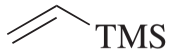
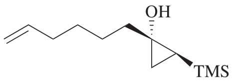
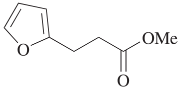
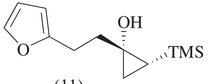
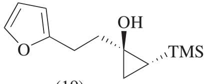
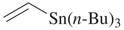
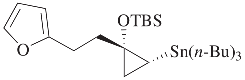
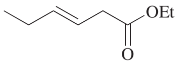
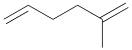
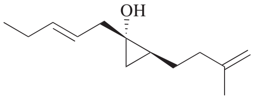
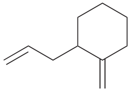
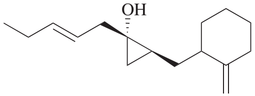
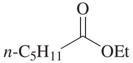
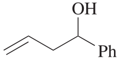
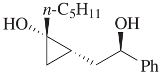
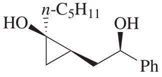
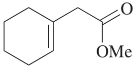
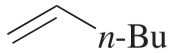
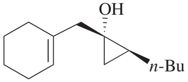
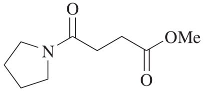
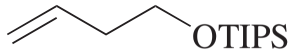
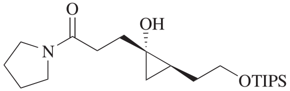
C_7			*c*-C_6H_{11}MgCl (4.5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt		(72)	60
C_8		$CH_2{=}CH_2$	*i*-PrMgCl (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), –78°; then rt		(43–69)	326
			*c*-C_6H_{11}MgCl (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt		(55)	60, 152
			*c*-C_5H_9MgCl (4.5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt		(53–77)	152
			*c*-C_6H_{11}MgCl (4.5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt		(46)	60
			*i*-PrMgCl (2.9 eq), ClTi(O*i*-Pr)$_3$ (1.5 eq), Et_2O, –60° to rt		(62) 81:19 dr	69
			*i*-PrMgCl (2.9 eq), ClTi(O*i*-Pr)$_3$ (1.5 eq), Et_2O, –60° to rt		(62) 88:12 dr	69, 357

TABLE 3. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		c-C_6H_{11}MgCl (4.5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (11) +  (19)	358
		1. c-C_5H_9MgCl (4–5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF 2. TBSCl	 (51)	358
		c-C_5H_9MgCl (excess), ClTi(Oi-Pr)$_3$ (1 eq), THF	 (56)	350
		c-C_5H_9MgCl (excess), ClTi(Oi-Pr)$_3$ (1 eq), THF	 (44)	350
		1. Ti(Oi-Pr)$_4$ (1.1 eq), PhMe, vacuum, rt to 40° 2. c-C_5H_9MgCl (4 eq), THF, rt	 **I** +  **II** **I** + **II** (62) dr 8.0:1	74
C_9 		c-C_6H_{11}MgCl (4.5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (56)	60
		c-C_5H_9MgCl (5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF	 (58)	79

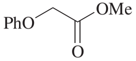
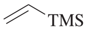
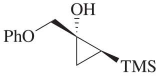
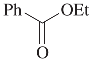
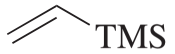
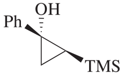
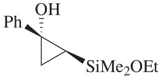
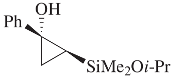
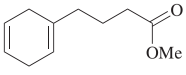
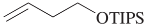
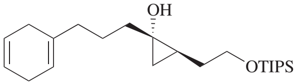
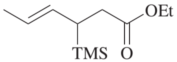
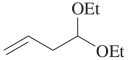
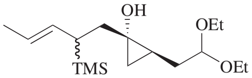
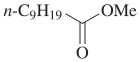
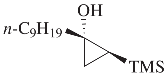
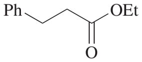
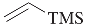
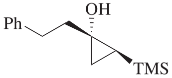
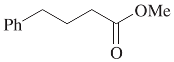
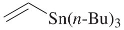
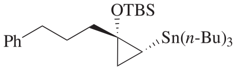
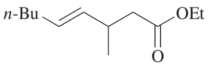
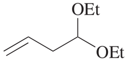
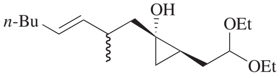
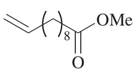
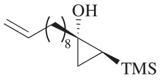
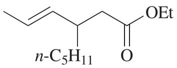
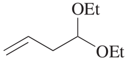
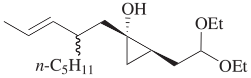
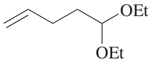
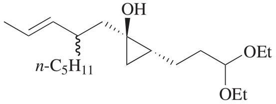
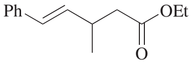
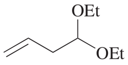
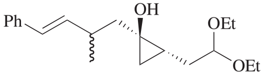
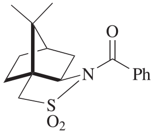
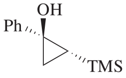
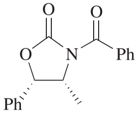
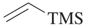
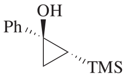
C_9			i-PrMgCl (2.9 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), Et_2O, –60 to –25°		(55) dr 88:12	69
			i-PrMgCl (2.9 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), Et_2O, –60 to –25°		(88) dr 93:7	357
			i-PrMgCl (2.9 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), Et_2O, –60 to –25°		(48) dr 65:35	357
			i-PrMgCl (2.9 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), Et_2O, –60 to –25°		(73) dr 85:15	69, 357
C_{11}			c-C_6H_{11}MgCl (4.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, rt		(64)	60
			c-C_5H_9MgCl (excess), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt		(43–54)	350
			i-PrMgCl (2.9 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), Et_2O, –60° to rt		(74) dr 88:12	69, 357
			i-PrMgCl (2.9 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), Et_2O, –60° to –25°		(76) 81:19 dr	69, 357
			1. c-C_5H_9MgCl (4 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, Et_2O, rt 2. TBSCl		(43)	358

TABLE 3. CYCLOPROPANATION OF ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		c-C_5H_9MgCl (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF	 (43–54)	350
		i-PrMgCl (2.9 eq), $ClTi(Oi$-$Pr)_3$ (1.5 eq), Et_2O, –60 to –25°	 (81) dr 87:13	69
C_{13} 		c-C_5H_9MgCl (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 (43–54)	350
		c-C_5H_9MgCl (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 (43–54)	350
C_{14} 		c-C_5H_9MgCl (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 (43–54)	350
C_{17} 		i-PrMgCl (2.9 eq), $ClTi(Oi$-$Pr)_3$ (1.5 eq), Et_2O, –60 to 0°	 (80) 0% ee	69
		i-PrMgCl (2.9 eq), $ClTi(Oi$-$Pr)_3$ (1.5 eq), Et_2O, –60 to 0°	 (60) 50% ee	69

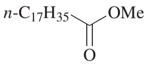
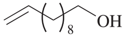
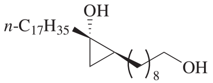
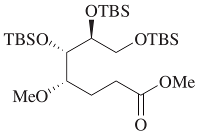
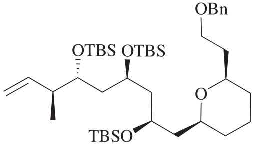
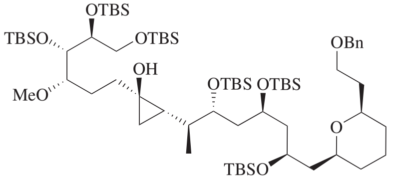
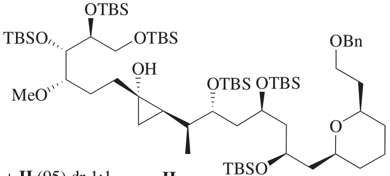
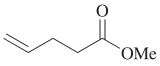
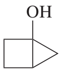
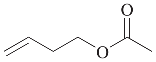
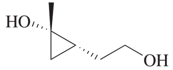
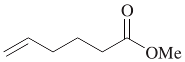
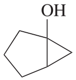
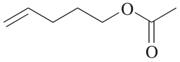
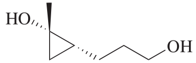
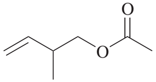
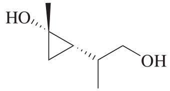
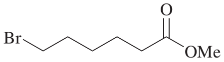
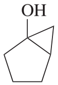
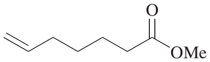
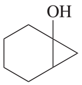
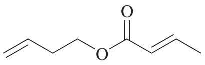
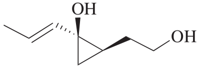
C_{19}			c-$C_6H_{11}MgBr$ (6 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et_2O, THF, rt		(>56)	355
C_{27}			c-$C_6H_{11}MgBr$ (4.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt	 **I** +  **II** **I** + **II** (95) dr 1:1		359

TABLE 4. INTRAMOLECULAR CYCLOPROPANATION OF ALKENOATES OR ALKENYL ESTERS WITH ALKOXYTITANACYCLOPROPANES

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	n-BuMgCl (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et$_2$O, rt	 (0)	55
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (93) dr 58:42	58
C_7 	RMgCl (3–5 eq), ClTi(O*i*-Pr)$_3$ (0.7–1 eq), THF or Et$_2$O, rt	 R *n*-Bu (71) *c*-C$_5$H$_9$ (55)	55, 81, 313
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 2°	 (61) dr 55:45	58
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (74) >97:3 dr	58
	Mg (2 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (16)	62
C_8 	*n*-BuMgCl or *c*-C$_5$H$_9$MgCl (3–5 eq), ClTi(O*i*-Pr)$_3$ (0.5–1 eq), THF or Et$_2$O, rt	 (55–62)	55, 81
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (73–78)	37, 58, 349

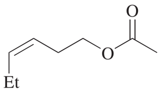
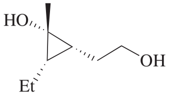
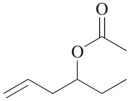
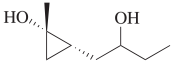
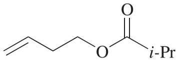
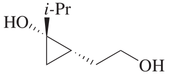
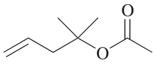
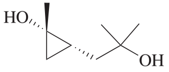
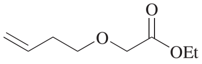
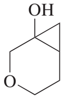
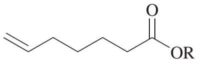
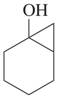
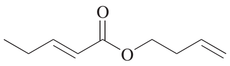
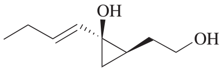
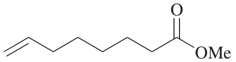
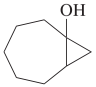
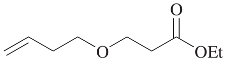
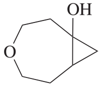
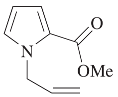
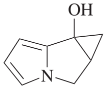
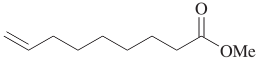
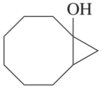
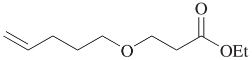
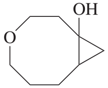
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), THF, –45 to 0°	 (<5)	58
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 **I** (33) dr 41:59	58
	i-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 20°	**I** (70) dr 95:5	58
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (88) dr 88:12	58
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), THF, –45 to 0°	 **I** (28) dr 47:53	58
	i-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), THF, –45 to 20°	**I** (78) dr 91:9	58
	*c*-C$_6$H$_{11}$MgCl (4 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, rt	 (35)	57
C$_{8–9}$			
	*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 R Me (57) Et (52)	56

TABLE 4. INTRAMOLECULAR CYCLOPROPANATION OF ALKENOATES OR ALKENYL ESTERS WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	i-PrMgBr (4 eq), Ti(Oi-Pr)$_4$ (2 eq), Et$_2$O, –40 to 0°	 **I** (69)	37
	i-PrMgBr (4 eq), Ti(TADDOL)$_2$ (2 eq), Et$_2$O, –40 to 0°	**I** (20) 22% ee	37
	n-BuMgCl or c-C$_5$H$_9$MgCl (3–5 eq), ClTi(Oi-Pr)$_3$ (0.5–1 eq), THF or Et$_2$O, rt	 (11)	55, 81
	c-C$_6$H$_{11}$MgCl (4 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, rt	 (62)	57
	i-PrMgCl (2.6 eq), Ti(Oi-Pr)$_4$ (1.3 eq), Et$_2$O, –78° to rt	 (80)	230
C_{10}			
	n-BuMgCl (5 eq), ClTi(Oi-Pr)$_3$ (0.5 eq), Et$_2$O, rt	 (0)	55
	c-C$_6$H$_{11}$MgCl (4 eq), Ti(Oi-Pr)$_4$ (2 eq), THF, rt	 (49)	57

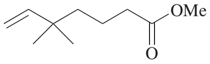
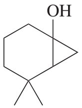
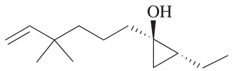
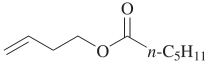
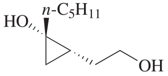
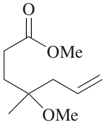
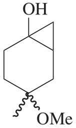
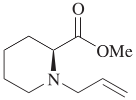
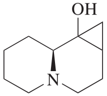
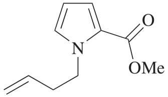
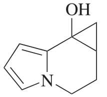
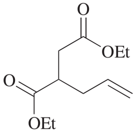
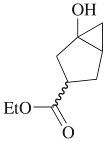
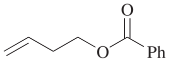
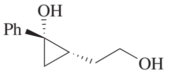
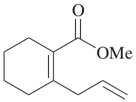
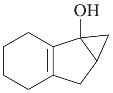
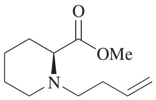
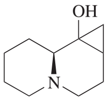
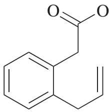
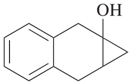
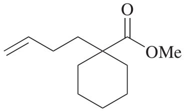
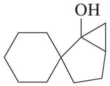
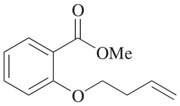
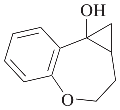
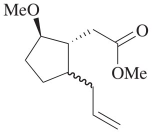
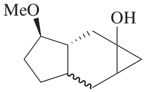
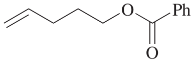
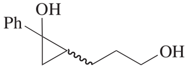
		*n*-BuMgCl (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et$_2$O, –45 to 0°	 (0) + 	(61)	55
		*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°		(95) dr 88:12	58
		*c*-C$_5$H$_9$MgCl (3–5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt		(85) dr 1.2:1	81
		*i*-PrMgCl (2.6 eq), Ti(O*i*-Pr)$_4$ (1.3 eq), Et$_2$O, –78 to 20°		(0)	230
		*i*-PrMgCl (2.6 eq), Ti(O*i*-Pr)$_4$ (1.3 eq), Et$_2$O, –78° to rt		(80)	230
C$_{11}$		*c*-C$_6$H$_{11}$MgCl (4 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, rt		(56) *cis*:*trans* = 53:47	360
		*i*-PrMgBr (4 eq), Ti(O*i*-Pr)$_4$ (2 eq) or *n*-BuMgCl (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et$_2$O, rt		(78–85) dr 7:1	55, 58
		*n*-BuMgCl (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et$_2$O, rt		(0)	55

TABLE 4. INTRAMOLECULAR CYCLOPROPANATION OF ALKENOATES OR ALKENYL ESTERS WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

	Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		c-C_5H_9MgCl (3–5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (0)	230
C_{12}		i-PrMgCl (4 eq), Ti(Oi-Pr)$_4$ (2 eq), Et_2O, –45 to 0°	 (98)	56
		i-PrMgBr (4 eq), Ti(Oi-Pr)$_4$ (2 eq), Et_2O, –45 to 0°	 (88)	56
		n-$C_6H_{11}MgCl$ (4 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (9)	57
		c-C_5H_9MgCl (3–5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (60) dr 1:1	81
		n-BuMgBr (5 eq), ClTi(Oi-Pr)$_3$ (0.5 eq), Et_2O, rt	 (15)	55

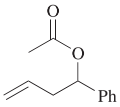
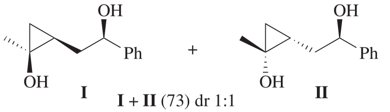
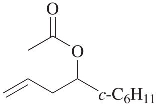
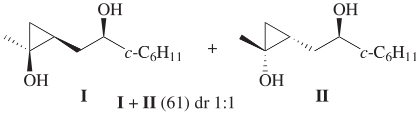
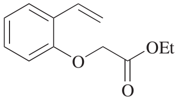
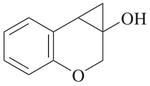
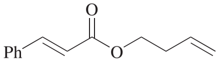
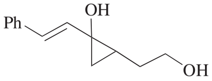
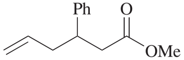
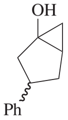
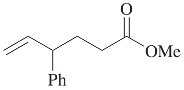
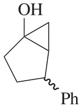
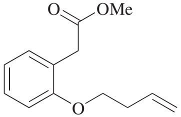
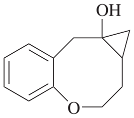
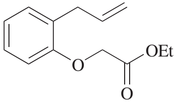
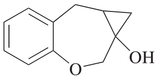
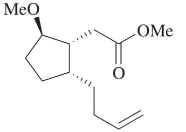
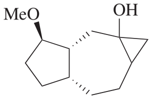
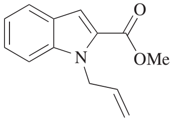
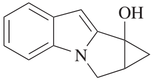
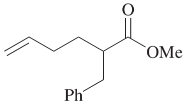
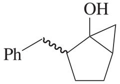
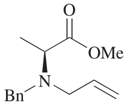
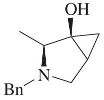
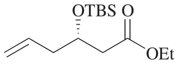
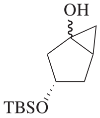
	c-C_5H_9MgCl (3–5 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, rt	 **I** + **II** (73) dr 1:1	74
	c-C_5H_9MgCl (excess), $Ti(Oi\text{-}Pr)_4$ or $ClTi(Oi\text{-}Pr)_3$, THF, rt	 **I** + **II** (61) dr 1:1	74
	c-$C_6H_{11}MgCl$ (4 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), THF, rt	 (46)	57
	i-PrMgBr (4 eq), $Ti(Oi\text{-}Pr)_4$ (2 eq), Et_2O, –40 to 0°	 (0)	37
	i-PrMgCl (4 eq), $Ti(Oi\text{-}Pr)_4$ (2 eq), Et_2O, –45 to 0°	 (83) dr 61:39	56
	i-PrMgCl (4 eq), $Ti(Oi\text{-}Pr)_4$ (2 eq), Et_2O, –45° to 0	 (76) dr 55:45	56
	c-$C_6H_{11}MgCl$ (4 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, rt	 (52)	57

TABLE 4. INTRAMOLECULAR CYCLOPROPANATION OF ALKENOATES OR ALKENYL ESTERS WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	c-C_6H_{11}MgCl (4 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (47)	57
	c-C_5H_9MgCl (3–5 eq), ClTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (40) dr 1:1	81
	*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 **I** (75)	56
	i-PrMgCl (2.6 eq), Ti(O*i*-Pr)$_4$ (1.3 eq), Et$_2$O, –78 to 20°	**I** (94)	230
C_{14} 	*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (77) dr 66:34	56
	*i*-PrMgCl (5 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et$_2$O, THF, 20°	 (64) dr 68:32	361, 362
	*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45° to rt	 (76)	363

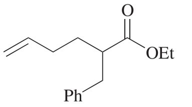
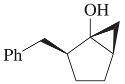
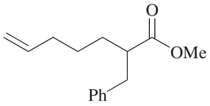
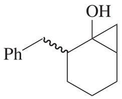
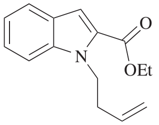
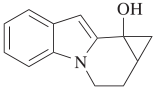
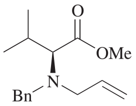
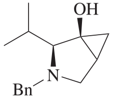
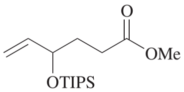
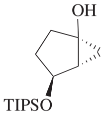
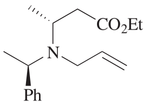
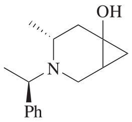
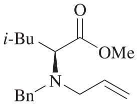
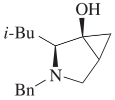
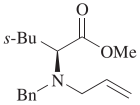
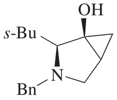
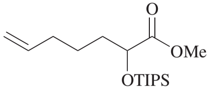
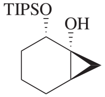
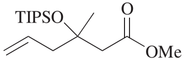
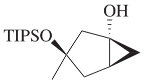
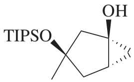
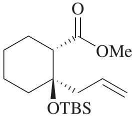
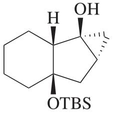
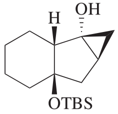
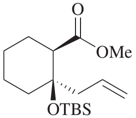
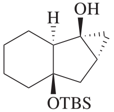
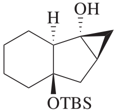
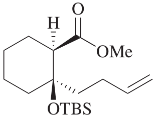
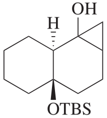
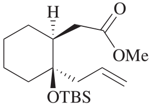
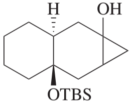
C_{15}		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (77) dr 66:34	59
		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (73) dr 89:11	56
		*i*-PrMgCl (2.6 eq), Ti(O*i*-Pr)$_4$ (1.3 eq), Et$_2$O, –78 to 20°	 (74)	230
C_{16}		*i*-PrMgCl (5 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et$_2$O, THF, 20°	 (75) dr 72:28	361, 362
		*n*-BuMgCl (5 eq), ClTi(O*i*-Pr)$_3$ (0.5 eq), Et$_2$O, rt	 (14)	55
C_{17}		*i*-PrMgCl (2.6 eq), Ti(O*i*-Pr)$_4$ (1.3 eq), Et$_2$O, –78 to 20°	 (73) dr 56:44	230
		*i*-PrMgCl (5 eq), Ti(O*i*-Pr)$_4$ (0.1 eq), Et$_2$O, THF, 20°	 (80) dr 64:36	361, 362

TABLE 4. INTRAMOLECULAR CYCLOPROPANATION OF ALKENOATES OR ALKENYL ESTERS WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

	Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		i-PrMgCl (5 eq), Ti(Oi-Pr)$_4$ (0.1 eq), Et$_2$O, THF, 20°	 (79) dr 71:29	361, 362
		n-BuMgCl (5 eq), ClTi(Oi-Pr)$_3$ (0.5 eq), Et$_2$O, rt	 (76) dr 2:1	55
		n-BuMgCl (5 eq), ClTi(Oi-Pr)$_3$ (0.5 eq), Et$_2$O, rt	 +  (58) dr 7:2	55
		c-C$_5$H$_9$MgCl or n-BuMgCl (3–5 eq), ClTi(Oi-Pr)$_3$ (0.5–1 eq), THF or Et$_2$O, rt	 +  (70–79) dr 2:1	55, 81
		c-C$_5$H$_9$MgCl or n-BuMgCl (3–5 eq), ClTi(Oi-Pr)$_3$ (0.5–1 eq), THF or Et$_2$O, rt	 +  (42) dr 3:2	55, 81
C_{18}		c-C$_5$H$_9$MgCl (3–5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (86) dr 9:1	81
		c-C$_5$H$_9$MgCl (3–5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (78) dr 1.3:1	81

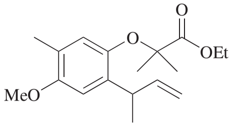
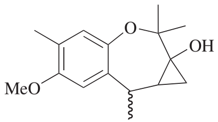
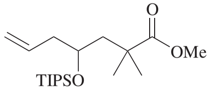
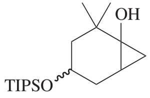
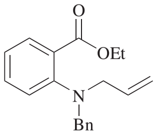
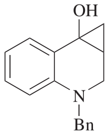
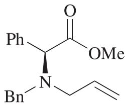
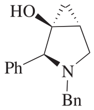
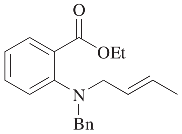
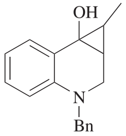
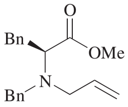
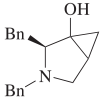
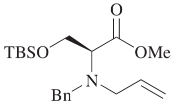
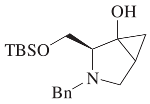
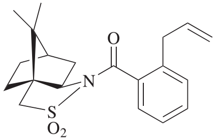
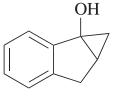
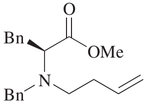
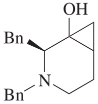
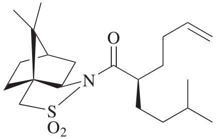
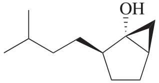
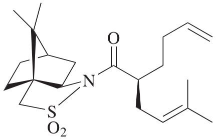
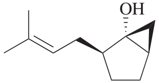
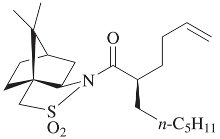
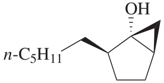
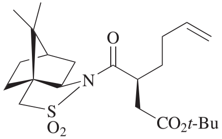
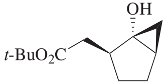
		c-$C_6H_{11}MgCl$ (4 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, THF, rt	 (43) dr 1:1	364, 365
C_{19}		n-BuMgCl (5 eq), $ClTi(Oi\text{-}Pr)_3$ (0.5 eq), THF or Et_2O, rt	 (75) dr 1:1	55
		i-PrMgCl (4 eq), $Ti(Oi\text{-}Pr)_4$ (2 eq), THF, –78 to 20°	 (94)	56, 230
		i-PrMgCl (5 eq), $Ti(Oi\text{-}Pr)_4$ (0.1 eq), Et_2O, THF, 20°	 (76) dr 59:41	361
C_{20}		i-PrMgCl (2 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), Et_2O, –78 to 20°	 (trace)	230
		i-PrMgCl (2.6 eq), $Ti(Oi\text{-}Pr)_4$ (1.3 eq), Et_2O, –78 to 20°	 (75) dr 73:27	230
		i-PrMgCl (2.6 eq), $Ti(Oi\text{-}Pr)_4$ (1.3 eq), Et_2O, –45° to rt	 (86) dr 3:1	156, 230

TABLE 4. INTRAMOLECULAR CYCLOPROPANATION OF ALKENOATES OR ALKENYL ESTERS WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

	Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (90) 32% ee	59
C_{21}		*i*-PrMgCl (2.6 eq), Ti(O*i*-Pr)$_4$ (1.3 eq), Et$_2$O, –45° to rt	 (76) dr 92:8	230
		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (80) dr >95:5	59
		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (87) dr >95:5	59
C_{22}		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (58) dr >95:5	59
		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (56) dr 92:8	59

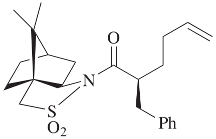
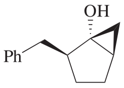
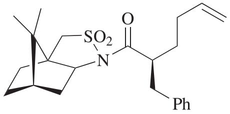
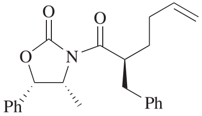
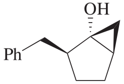
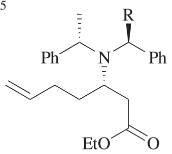
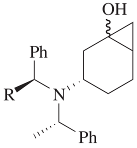
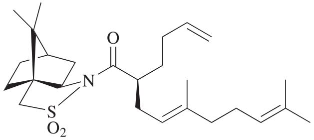
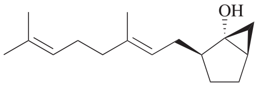
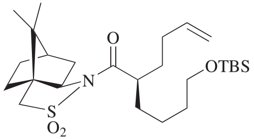
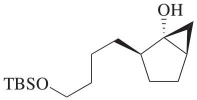
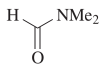
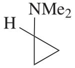
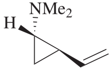
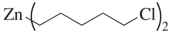
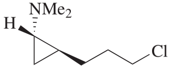
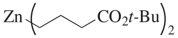
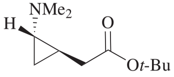
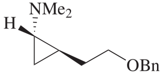
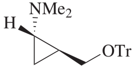
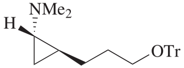
C_{23}		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 **I** (86) dr >99:1	59
		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	**I** (78) 92:8 dr	59
		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (38) ds 74:26	59
$C_{24–25}$		*i*-PrMgCl (2 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O	 R H (76) Me (63)	366
C_{26}		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (74) dr >95:5	59
		*i*-PrMgCl (4 eq), Ti(O*i*-Pr)$_4$ (2 eq), Et$_2$O, –45 to 0°	 (84) dr >95:5	59

TABLE 5. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES

Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et_2O, THF, 20–45°	 (73)	75
	CH_2=CH(CH_2)$_2$MgBr (1.1 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, –78° to rt	 (57) dr 17:1	62
	 (1 eq), Me_2Ti(O*i*-Pr)$_2$ (1 eq), MeMgCl (1.1 eq), THF, –30 to 20°	 (65) dr 1.2:1	80
	 (1 eq), Me_2Ti(O*i*-Pr)$_2$ (1 eq), MeMgCl (1.1 eq), THF, –30 to 20°	 (63) dr 1.3:1	80
	BnO(CH_2)$_4$MgBr (1.1 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, –78° to rt	 (54) dr 1.1:1	62
	TrO(CH_2)$_3$MgBr (1.1 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, –78° to rt	 (18) dr >25:1	62
	TrO(CH_2)$_5$MgBr (1.1 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, –78° to rt	 (53) dr 1.8:1	62

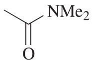
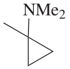
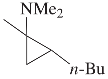
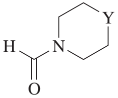
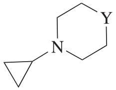
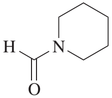
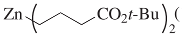
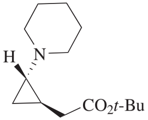
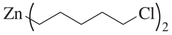
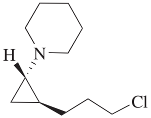
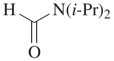
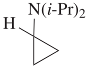
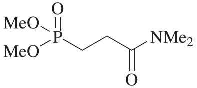
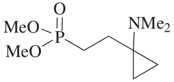
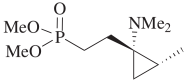
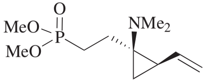
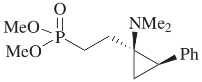
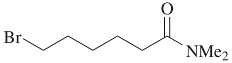
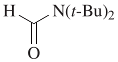
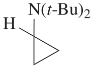
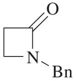
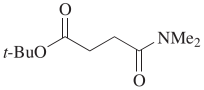
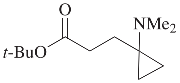
C_4		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 18–20°	 **I** (<30)	75
		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78 to 20°	**I** (56)	75
		n-C$_6$H$_{13}$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to rt	 **I** (38) dr >25:1	62
		n-C$_6$H$_{13}$MgBr (2.2 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, –78° to rt	**I** (51)	62
$C_{5–6}$		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (*x* eq), Et$_2$O, THF, 20–45°	 Y *x* O 1 (74) C 1.1 (74)	75
C_6		 (1 eq), Me$_2$Ti(O*i*-Pr)$_2$ (1 eq), MeMgCl (1.1 eq), THF, –30 to 20°	 (52) dr 1.4:1	80
		 (1 eq), Me$_2$Ti(O*i*-Pr)$_2$ (1 eq), MeMgCl (1.1 eq), THF, –30° to 20°	 (67) dr 1.2:1	80
C_7		EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (3 eq), THF, –78 to 20°	 (76)	75

TABLE 5. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	EtMgBr (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (79)	48
	n-PrMgBr (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (81) dr 6:1	48
	CH$_2$=CHCH$_2$CH$_2$MgBr (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (86) dr 1.6:1	48
	Ph(CH$_2$)$_2$MgBr (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (82) dr 1.4:1	48
C_8 	Mg (2 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, rt	 (28)	62
C_9 	EtMgBr (6 eq), Ti(O*i*-Pr)$_4$ (3 eq), THF, –78°; then reflux	 (20)	75
C_{10} 	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, 20°	 (21)	62
	EtMgBr (1.7–2.0 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, rt	 (30)	80

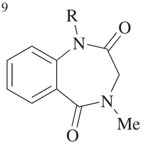
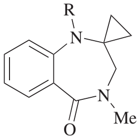
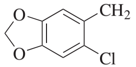
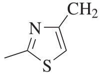
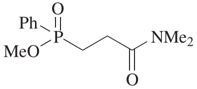
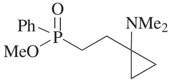
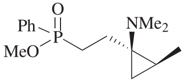
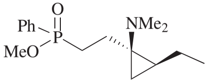
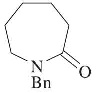
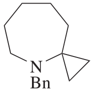
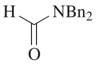
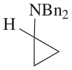
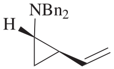
C$_{11-19}$ 	EtMgBr (2.5 eq), MeTi(O*i*-Pr)$_3$ (5 eq), THF, rt	 R Me (16) Et (15) *i*-Pr (25) $CH_2{=}CHCH_2$ (32) *c*-$C_3H_5CH_2$ (20) *c*-$C_4H_7CH_2$ (33) Bn (43) 4-$MeOC_6H_4CH_2$ (20) 3-$MeOC_6H_4CH_2$ (15) 3,4-$(MeO)_2C_6H_3CH_2$ (8)  (8)  (24)	367
C$_{12}$ 	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, 0° to rt	 (47)	48
	n-PrMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, 0° to rt	 (39) dr 8.5:1	48
	n-BuMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, 0° to rt	 (42) dr 10:1	48

TABLE 5. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, 65°	 **I** (33)	62
	EtMgBr (1.1 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, 65°	**I** (47)	62
C_{15} 	EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), Et$_2$O, THF, 20–45°	 **I** (69)	75
	EtMgBr (1.7–2.0 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, rt	**I** (90)	80
	Et$_2$Zn (*x* eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), MOR (*y* eq), THF, rt	**I** *x* MOR *y* **I** 2 — — (21) 2 NaO*i*-Pr 1 (52) 2 NaO*i*-Pr 2 (89) 2 LiO*i*-Pr 2 (84) 2 NaOMe 2 (10) 2 NaOEt 2 (82) 2 NaO*t*-Bu 2 (76) 1 NaO*i*-Pr 2 (82) 0.5 NaO*i*-Pr 2 (43)	94
	CH$_2$=CH(CH$_2$)$_2$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to rt	 **I** (42) dr >25:1	62
	CH$_2$=CH(CH$_2$)$_2$MgBr (1.1 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, –78° to rt	**I** (54)	62

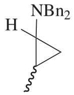
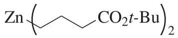
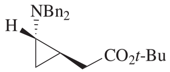
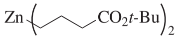
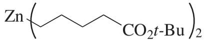
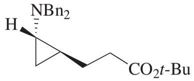
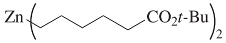
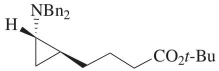
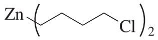
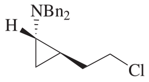
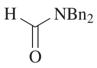
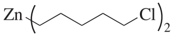
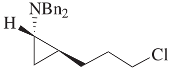
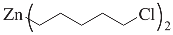
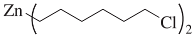
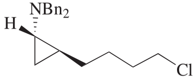
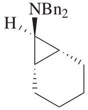
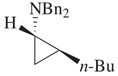
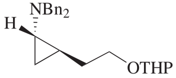
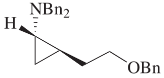
CH_2=CH(CH_2)$_2$MgBr (1.5 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, rt	**I** (71)	319
n-PrMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	 (63) dr 1:1	75
 (1 eq), MeMgCl (5 eq), Cl_2Ti(O*i*-Pr)$_2$ (1 eq), THF, –30 to 20°	 **I** (49) dr 1.1:1	80
 (1 eq), MeLi (2.2 eq), MeMgCl (1.1 eq), Me_2Ti(O*i*-Pr)$_2$ (1 eq), THF, –30° to rt	**I** (60) dr 1.8:1	80
 (1 eq), MeMgCl (1.1 eq), Me_2Ti(O*i*-Pr)$_2$ (1 eq), THF, –30° to rt	 (40) dr 1.2:1	80
 (1 eq), MeMgCl (1.1 eq), Me_2Ti(O*i*-Pr)$_2$ (1 eq), THF, –30° to rt	 (24) dr 1.1:1	80
 (1 eq), MeMgCl (1.1 eq), Me_2Ti(O*i*-Pr)$_2$ (1 eq), THF, –30° to rt	 (27)	80

TABLE 5. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	 (1 eq), MeMgCl (5 eq), $Cl_2Ti(Oi\text{-}Pr)_2$ (1 eq), THF, –30 to 20°	 **I** (61) dr 1.4:1	80
	 (1 eq), MeMgCl (1.1 eq), $Me_2Ti(Oi\text{-}Pr)_2$ (1 eq), THF, –30 to 20°	**I** (55) dr 1.1:1	80
	 (1 eq), MeMgCl (5 eq), $Cl_2Ti(Oi\text{-}Pr)_2$ (1 eq), THF, –30 to 20°	 (57) dr 1.1:1	80
	$c\text{-}C_6H_{11}MgBr$, $MeTi(Oi\text{-}Pr)_3$ (1 eq), THF, 60°	 (38)	62
	$n\text{-}C_6H_{13}MgBr$ (2.5 eq), $Ti(Oi\text{-}Pr)_4$ (1 eq), THF, –78° to reflux	 (52) dr 2.3:1	75
	$THPO(CH_2)_4MgBr$ (1.1 eq), $MeTi(Oi\text{-}Pr)_3$ (1 eq), THF, –78° to rt	 (34) dr 2.1:1	62
	$BnO(CH_2)_4MgBr$ (1.7–2.0 eq), $MeTi(Oi\text{-}Pr)_3$ (1.2 eq), THF, Et_2O, rt	 (67) dr 1.7:1	368

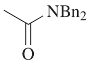
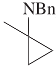
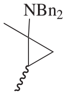
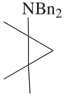
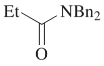
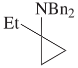
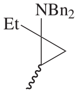
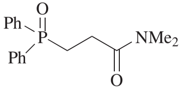
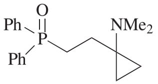
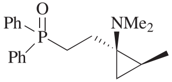
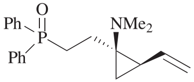
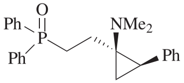
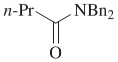
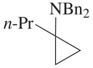
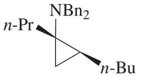
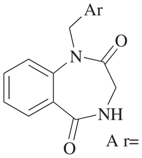
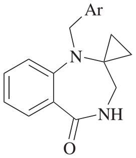
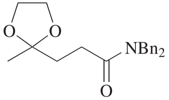
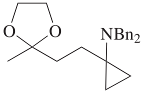
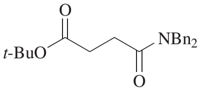
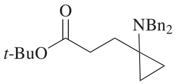
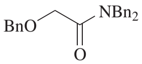
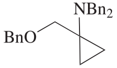
C_{16}		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	 (60)	75
		n-PrMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	 (50)	75
		i-BuMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	 (51)	75
C_{17}		EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	 (63)	75
		n-PrMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	 (38)	75
		EtMgBr (2.4 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (83)	48
		n-PrMgBr (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (80) dr 3.5:1	48
		CH$_2$=CHCH$_2$CH$_2$MgBr (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (83) dr 3:1	48
		Ph(CH$_2$)$_2$MgBr (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt	 (67) dr 1.6:1	48

TABLE 5. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	EtMgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	 (52)	75
	n-C_6H_{13}MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to rt	 **I** (35) dr 10:1	62
	n-C_6H_{13}MgBr (2.5 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to reflux	**I** (35)	75
	n-C_6H_{13}MgBr (1.1 eq), MeTi(O*i*-Pr)$_3$ (1 eq), THF, –78° to rt	**I** (47)	62
 A r= 3,4-MeOC_6H_3	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1 eq), THF, –78° to rt	 (10)	367
C_{21} 	EtMgBr (1.7–2.0 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et_2O, rt	 (84)	368
C_{22} 	EtMgBr, MeTi(O*i*-Pr)$_3$, THF, rt	 (37)	80
C_{23} 	EtMgBr (1.7–2.0 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), THF, Et_2O, rt	 (48)	368

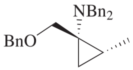
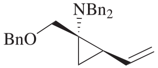
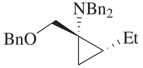
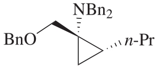
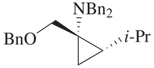
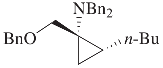
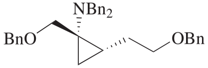
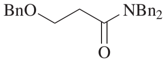
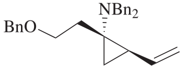
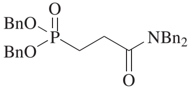
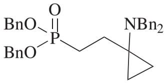
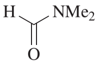
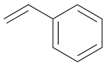
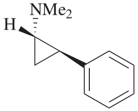
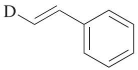
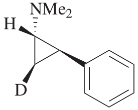
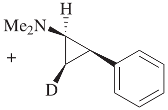
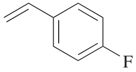
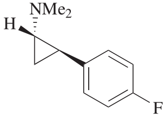
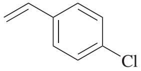
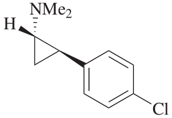
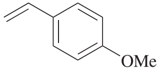
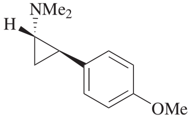
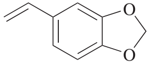
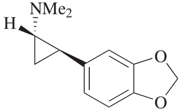
	n-PrMgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(37) dr 3:1	368
	CH$_2$=CH(CH$_2$)$_2$MgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(49) dr 3:1	368
	n-BuMgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(48) dr 5:1	368
	n-C$_5$H$_{11}$MgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(34) dr 3:1	368
	i-C$_5$H$_{11}$MgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(42) dr 3:1	368
	n-C$_6$H$_{13}$MgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(33) dr 2:1	368
	BnO(CH$_2$)$_4$MgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(40) dr 3:1	368
C$_{24}$ 	CH$_2$=CH(CH$_2$)$_2$MgBr (1.7–2.0 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(56) dr 2.5:1	369
C$_{31}$ 	EtMgBr (2 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et$_2$O, rt		(62)	48

TABLE 6. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE

Carboxamide	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		c-C_5H_9MgBr, $ClTi(Oi\text{-}Pr)_3$, THF, 0° to rt	 (78)	370
		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, Et_2O, 0° to rt	 (36) +  (12)	30
		c-C_5H_9MgBr (excess), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt	 (78)	370
		c-C_5H_9MgBr (excess), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt	 (49)	370
		c-C_5H_9MgBr (excess), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt	 (52)	370
		c-C_5H_9MgBr (excess), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt	 (45)	370

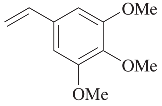
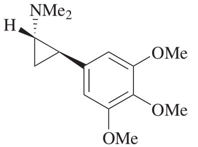
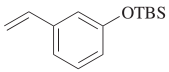
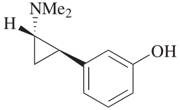
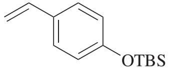
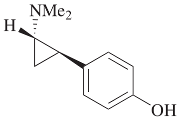
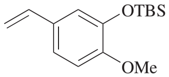
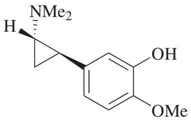
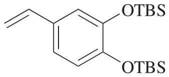
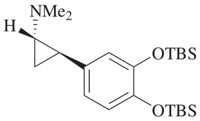
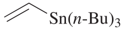
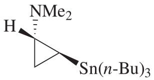
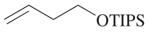
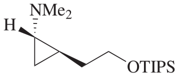
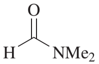
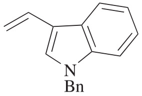
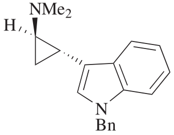
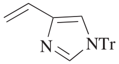
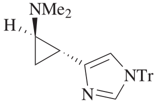
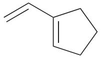
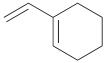
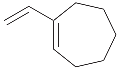
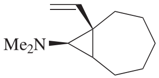
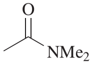
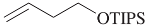
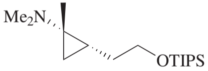
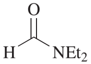
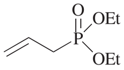
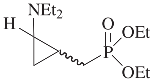
	c-C_5H_9MgBr (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, 0° to rt		(42)	370
	1. c-C_5H_9MgBr (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, 0° to rt 2. TBAF, 3 Å MS, THF		(58)	370
	1. c-C_5H_9MgBr (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, 0° to rt 2. TBAF, 3 Å MS, THF		(74)	370
	1. c-C_5H_9MgBr (excess), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, 0° to rt 2. TBAF, 3 Å MS, THF		(65)	370
	c-C_5H_9MgBr, $ClTi(Oi$-$Pr)_3$, THF, 0° to rt		(55)	370
	c-$C_6H_{11}MgBr$ (2.5 eq), $MeTi(Oi$-$Pr)_3$ (2 eq), THF, rt		(88)	371
	c-C_5H_9MgCl (4.5 eq), $ClTi(Oi$-$Pr)_3$ (1.5 eq), THF, rt		(61) dr 2.2:1	77

TABLE 6. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxamide	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		c-C_5H_9MgBr (excess), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt	 (52)	370
		c-C_5H_9MgBr (excess), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt	 (65)	370
		c-$C_6H_{11}MgBr$ (2–3.6 eq), $MeTi(Oi\text{-}Pr)_3$ (1.2 eq), THF, Et_2O, rt	 (72)	372
		c-$C_6H_{11}MgBr$ (2–3.6 eq), $MeTi(Oi\text{-}Pr)_3$ (1.2 eq), THF, Et_2O, rt	 (63)	372
		c-$C_6H_{11}MgBr$ (2–3.6 eq), $MeTi(OPr\text{-}i)_3$ (1.2 eq), THF, Et_2O, rt	 (58)	372
C_4 		c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, rt	 (68) dr 6.3:1	77
C_5 		c-$C_6H_{11}MgBr$, $Ti(Oi\text{-}Pr)_4$, THF, Et_2O, rt	 (36) dr 1.6:1	48

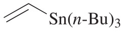
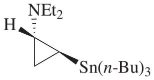
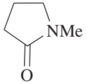
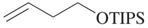
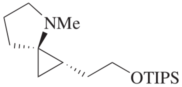
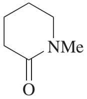
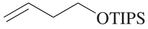
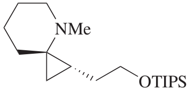
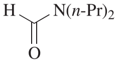
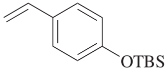
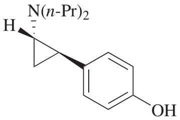
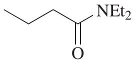
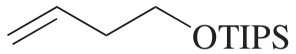
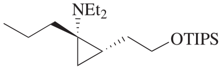
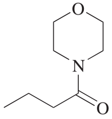
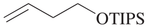
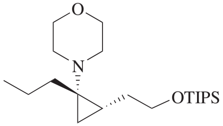
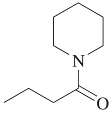
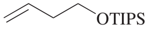
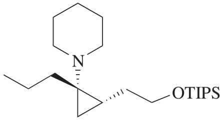
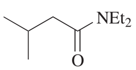
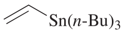
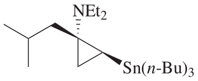
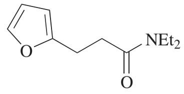
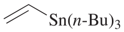
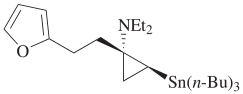
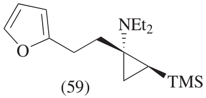
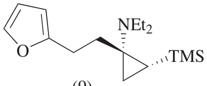
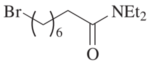
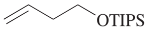
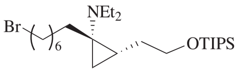
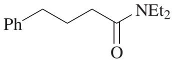
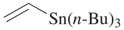
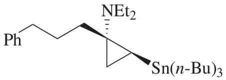
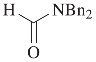
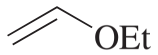
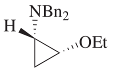
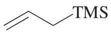
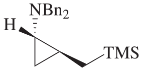
			c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1.1 eq), THF, rt		(57)	358
			c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, rt		(21)	77
C_6			c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1.1 eq), THF, rt		(79) dr 6.2:1	77
C_7			1. c-C_5H_9MgBr (excess), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, 0° to rt 2. TBAF, 3 Å MS, THF		(31)	370
C_8			c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, rt		(56) dr 5.3:1	77
			c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, rt		(77) dr 3.1:1	77
C_9			c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, rt		(69) dr 7.3:1	77

TABLE 6. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

	Carboxamide	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			c-C_5H_9MgCl (4.5 eq), ClTi(Oi-Pr)$_3$ (1.1 eq), THF, rt	 (66)	358
C_{11}			c-C_5H_9MgCl (4.5 eq), ClTi(Oi-Pr)$_3$ (1.1 eq), THF, rt	 (68)	358
			c-$C_6H_{11}MgBr$ (4.5 eq), ClTi(Oi-Pr)$_3$ (1.1 eq), THF, rt	 (59) +  (9)	358
C_{12}			c-C_5H_9MgCl (4.5 eq), ClTi(Oi-Pr)$_3$ (1.5 eq), THF, rt	 (60) dr 7.6:1	77
C_{14}			c-C_5H_9MgCl (4.5 eq), ClTi(Oi-Pr)$_3$ (1.1 eq), THF, rt	 (71)	358
C_{15}			c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, Et_2O, 0° to rt	 (4)	82
			c-$C_6H_{11}MgBr$ (1.5–2.4 eq), MeTi(Oi-Pr)$_3$ (1–1.5 eq), THF, Et_2O, rt	 (28)	82

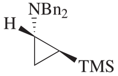
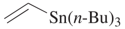
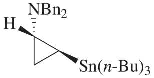
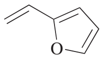
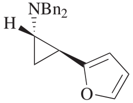
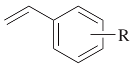
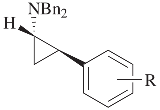
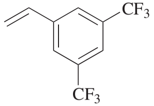
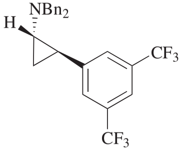
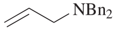
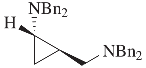
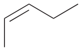
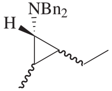
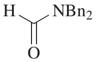
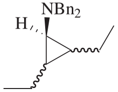
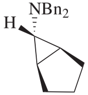
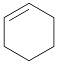
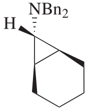
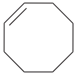
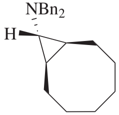
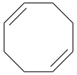
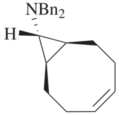
	c-$C_6H_{11}MgBr$ (1.5–2.4 eq), $MeTi(Oi\text{-}Pr)_3$ (1.0–1.5 eq), THF		(59)	82
	c-$C_6H_{11}MgBr$ (2.5 eq), $MeTi(Oi\text{-}Pr)_3$ (2 eq), THF, rt		(92)	371
	c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, Et_2O, 0° to rt		(43) dr 4:1	82
	c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, Et_2O, 0° to rt		R — dr H (66) 3.1:1 2-Br (45) 1.2:1 4-MeO (30) >98:2 2-CF_3 (11) 4:1 3-CF_3 (18) 1:0 4-CF_3 (46) 11.5:1	82
	c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, 0° to rt		(9) dr 16:1	82
	c-$C_6H_{11}MgBr$ (1.5–2.4 eq), $MeTi(Oi\text{-}Pr)_3$ (1–1.5 eq), THF, Et_2O, rt		(39) dr 4:1	82
	c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, 0° to rt		(26) dr 6:2:1	82

TABLE 6. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxamide	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, 0° to rt	 (13) dr 15:14:1	82
		c-C_5H_9MgBr (3.1 eq), Ti(Oi-Pr)$_4$ (1.0 eq), THF, PhH, rt to reflux	 **I** (88) dr >98:2	82
		c-$C_6H_{11}MgBr$ (2–2.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, Et_2O, rt	**I** (28) dr >98:2	82
		c-$C_6H_{11}MgBr$ (3.1 eq), Ti(Oi-Pr)$_4$ (1.0 eq), THF, PhH, rt to reflux	 (27) dr >98:2	82
		c-$C_8H_{15}MgBr$ (3.1 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, PhH, rt to reflux	 (33) dr >98:2	82
		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, PhH, rt to reflux	 **I** (11) dr >98:2	82

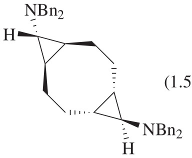
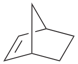
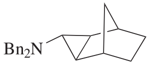
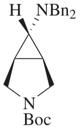
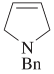
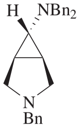
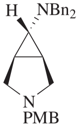
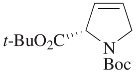
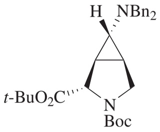
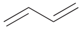
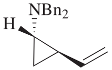
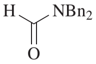
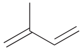
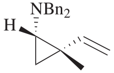
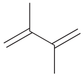
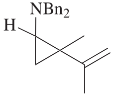
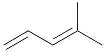
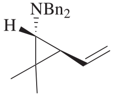
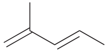
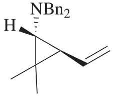
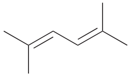
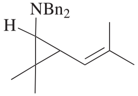
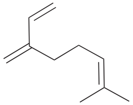
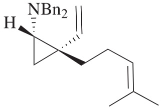
	c-$C_6H_{11}MgBr$ (2–2.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, Et_2O, rt	**I** (5.8) +  (1.5) dr >98:2	82
	c-$C_6H_{11}MgBr$ (2–2.5 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, Et_2O, rt	 (43) >98:2 dr	82
	c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, 0° to rt	 (90) dr >98:2	82
	c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, 0° to rt	 (87) dr >98:2	82
	c-$C_6H_{11}MgBr$ (3.3 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, 0° to reflux	 (68) dr >98:2	82
	c-$C_6H_{11}MgBr$ (2 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, Et_2O, rt	 (50) 95% de	373
	c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, –20° to rt	 (56) dr 2.7:1	374

TABLE 6. CYCLOPROPANATION OF CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE (*Continued*)

Carboxamide	Olefin	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{15} 		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, –20° to rt		(59) dr >98:2	374
		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, 0° to rt		(0)	374
		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, 0° to rt		(64) dr 5.3:1	374
		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, 0° to rt		(27) dr 3:1	374
		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, Et_2O, 0° to rt		(0)	82, 374
		c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), THF, 0° to rt		(51)	374

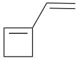
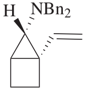
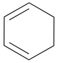
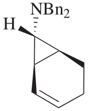
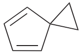
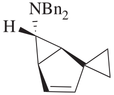
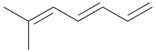
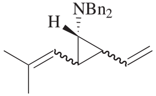
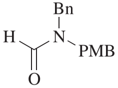
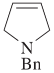
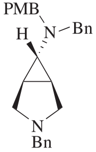
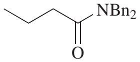
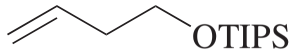
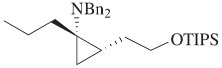
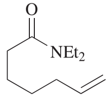
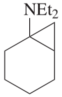
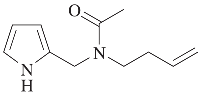
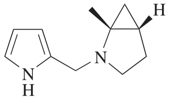
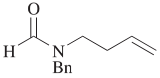
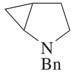
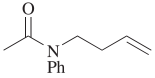
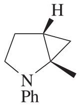
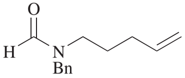
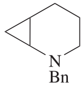
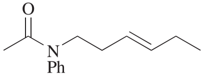
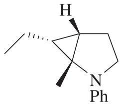
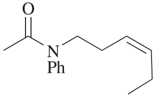
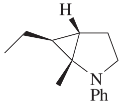
			c-$C_6H_{11}MgBr$ (2–3.6 eq), MeTi(Oi-Pr)$_3$ (1.2 eq), THF, rt	 (63)	372
			c-$C_6H_{11}MgBr$ (2–2.5 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, Et_2O, rt	 (58)	82
			c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, Et_2O, 0° to rt	 (trace)	82
			c-$C_6H_{11}MgBr$ (1.2 eq), MeMgCl (1.2 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, Et_2O, 0° to rt	 (54) dr 1.5:1.5:1	374
C_{16}			c-$C_6H_{11}MgBr$ (3.3 eq), Ti(Oi-Pr)$_4$ (1 eq), THF, 0° to reflux	 (67)	82
C_{18}			c-C_5H_9MgCl (4.5 eq), ClTi(Oi-Pr)$_3$ (1 eq), THF, rt	 (54) dr 1.3:1	77

TABLE 7. INTRAMOLECULAR CYCLOPROPANATION OF UNSATURATED CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES

	Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		c-C_5H_9MgCl (4.5 eq), $ClTi(Oi$-$Pr)_3$ (1.5 eq), THF, rt	 (64)	77
		1. n-BuLi, THF, –70° 2. TMSCl, –70 to 20° 3. c-C_5H_9MgCl (4.5 eq), $Ti(Oi$-$Pr)_4$ (1.5 eq), THF, rt	 (68)	213
C_{12}		c-$C_6H_{11}MgBr$ (3.3 eq), $Ti(Oi$-$Pr)_4$ (1.1 eq), THF, rt	 (84)	83
		c-C_5H_9MgCl (4.5 eq), $ClTi(Oi$-$Pr)_3$ (1.5 eq), THF, rt	 (93)	77
C_{13}		c-$C_6H_{11}MgBr$ (3.3 eq), $Ti(Oi$-$Pr)_4$ (1.1 eq), THF, rt	 (67)	83
C_{14}		c-C_5H_9MgCl (4.0 eq), $Ti(Oi$-$Pr)_4$ (1.5 eq), Et_2O, rt	 (24)	78
		c-C_5H_9MgCl (4.0 eq), $Ti(Oi$-$Pr)_4$ (1.5 eq), Et_2O, PhMe, rt	 (40)	78

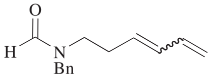
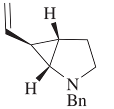
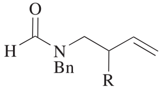
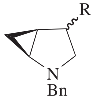
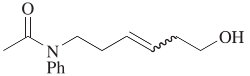
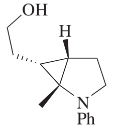
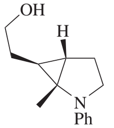
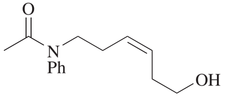
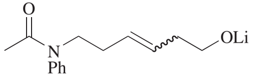
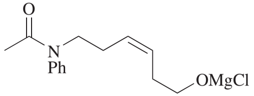
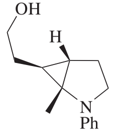
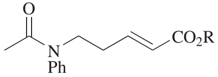
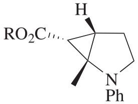
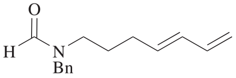
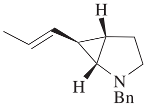
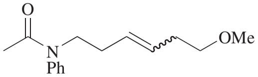
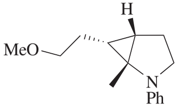
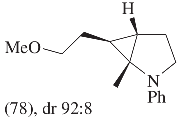
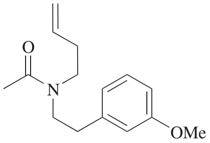
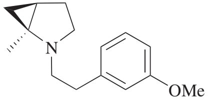
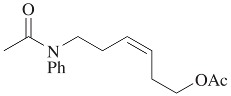
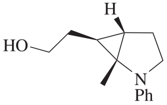
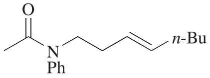
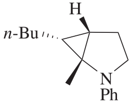
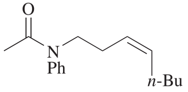
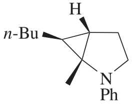
	c-C_6H_{11}MgBr (3.3 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, rt	 (23–32)	83
C_{14-17}			
	c-C_6H_{11}MgBr (3.3 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, rt	 R / *exo*/*endo* Et 3:1 (82) *i*-Pr 8:1 (77) *s*-Bu 10:1 (74) c-C_5H_9 5:1 (85)	83
C_{14}			
 (*E*)/(*Z*) = 75:25	c-C_5H_9MgCl (4.0 eq), Ti(O*i*-Pr)$_4$ (1.5 eq), Et$_2$O, rt	 **I** +  **II** **I** + **II** (9), dr 64:36	375
	c-C_5H_9MgCl (4.0 eq), Ti(O*i*-Pr)$_4$ (1.5 eq), Et$_2$O, rt	**II** (10)	375
 (*E*)/(*Z*) = 75:25	c-C_5H_9MgCl (4.0 eq), Ti(O*i*-Pr)$_4$ (1.5 eq), Et$_2$O, rt	**I** + **II** (17) dr 66:34	375
	c-C_5H_9MgCl (4.0 eq), Ti(O*i*-Pr)$_4$ (1.5 eq), PhMe, rt	 (21)	375
C_{14-17}			
	c-C_5H_9MgCl (4.0 eq), Ti(O*i*-Pr)$_4$ (1.5 eq), Et$_2$O, rt	 R Me (0) *t*-Bu (0)	375

TABLE 7. INTRAMOLECULAR CYCLOPROPANATION OF UNSATURATED CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	c-$C_6H_{11}MgBr$ (3.3 eq), Ti(Oi-Pr)$_4$ (1.1 eq), THF, rt	 (14)	83
 (E)/(Z) = 90:10	c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), Et_2O, rt	 **I** +  **II** **I** + **II** (78), dr 92:8	375
	c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.4 eq), THF, rt	 (87)	213
C_{16}			
	c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), PhMe, 20°	 (8)	375
	c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), Et_2O, rt	 (18)	375
	c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), Et_2O, rt	 (12)	375

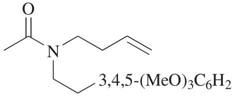
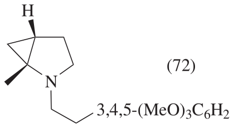
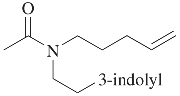
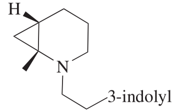
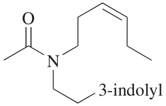
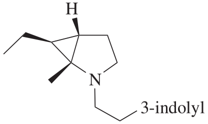
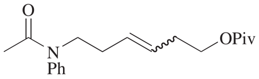
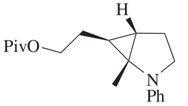
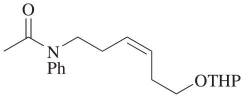
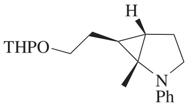
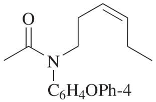
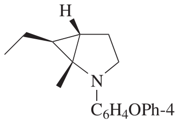
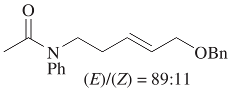
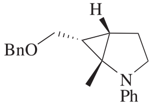
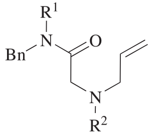
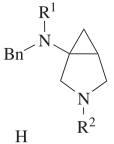
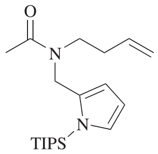
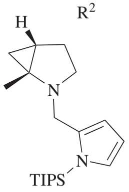
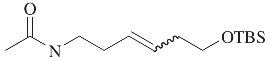
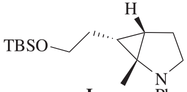
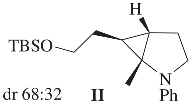
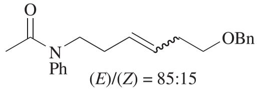
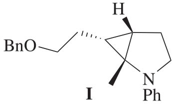
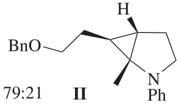
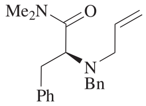
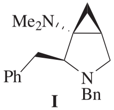
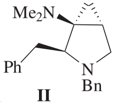
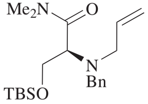
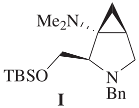
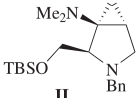
C_{17}		c-C_5H_9MgCl (4.5 eq), Ti(Oi-Pr)$_4$ (1.5 eq), THF, rt		(72)	213
		c-C_5H_9MgCl (4 eq), Ti(Oi-Pr)$_4$ (1.5 eq), THF, rt		(37)	213
C_{18}		c-C_5H_9MgCl (4 eq), Ti(Oi-Pr)$_4$ (1.5 eq), THF, rt		(20)	78
C_{19}		c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), PhMe, rt		(0)	375
		c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), PhMe, rt		(23)	375
C_{20}		c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), Et_2O, rt		(38)	78
	 (E)/(Z) = 89:11	c-C_5H_9MgCl (4.0 eq), Ti(Oi-Pr)$_4$ (1.5 eq), Et_2O, rt		(traces)	375

TABLE 7. INTRAMOLECULAR CYCLOPROPANATION OF UNSATURATED CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	c-$C_6H_{11}MgBr$ (5 eq), $MeTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, 20°	 R^1 R^2 Me Bn (56) Bn Me (66)	96
	c-C_5H_9MgCl (4.5 eq), $Ti(Oi\text{-}Pr)_4$ (1.5 eq), THF, rt	 (44)	213
 (*E*)/(*Z*) = 85:15	c-C_5H_9MgCl (4.0 eq), $Ti(Oi\text{-}Pr)_4$ (1.5 eq), Et_2O, rt	 **I** +  **II** **I** + **II** (38), dr 68:32	375
C_{21}  (*E*)/(*Z*) = 85:15	c-C_5H_9MgCl (4.0 eq), $Ti(Oi\text{-}Pr)_4$ (1.5 eq), Et_2O, rt	 **I** +  **II** **I** + **II** (53), dr 79:21	375
	c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, rt	 **I** +  **II** **I** + **II** (83), dr 72:28	376
	c-$C_6H_{11}MgBr$ (6 eq), $MeTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, 20°	 **I** +  **II** **I** + **II** (89), dr 2:1	96

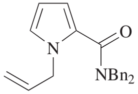
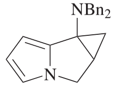
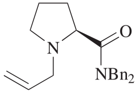
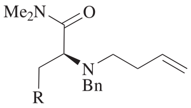
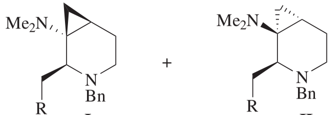
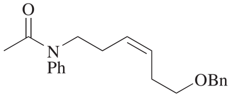
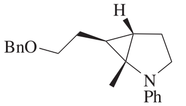
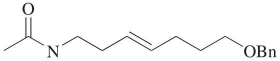
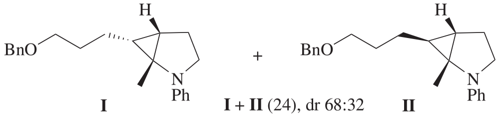
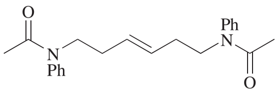
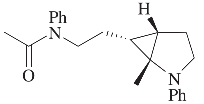
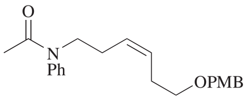
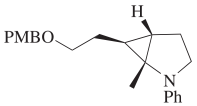
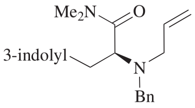
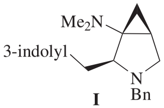
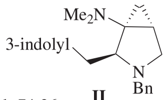
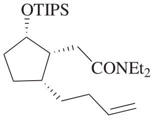
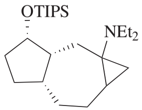
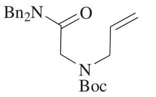
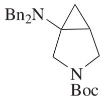
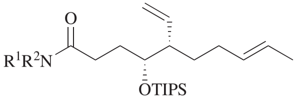
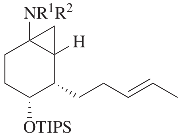
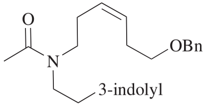
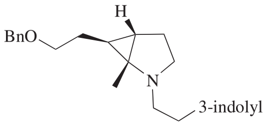
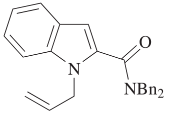
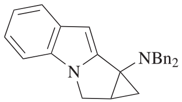
C_{22}		c-$C_6H_{11}MgBr$ (5 eq), $MeTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, rt		(78)	377
		c-$C_6H_{11}MgBr$ (5 eq), $MeTi(Oi\text{-}Pr)_3$ (1.5 eq), THF, rt	 **I** **I** + **II** (70), dr 2.9:1 **II**		377
		c-C_5H_9MgCl (4.5 eq), $ClTi(Oi\text{-}Pr)_3$ (1 eq), THF, rt	 **I** **II**	R, **I** + **II**, dr Ph (60) 9:1 TBSO (61) —	378
		c-C_5H_9MgCl (4.0 eq), $Ti(Oi\text{-}Pr)_4$ (1.5 eq), rt		Solvent Et_2O (44) toluene (50)	375
	 $(E)/(Z) = 80{:}20$	c-C_5H_9MgCl (4.0 eq), $Ti(Oi\text{-}Pr)_4$ (1.5 eq), Et_2O, rt	 **I** **I** + **II** (24), dr 68:32 **II**		375
		c-C_5H_9MgCl (4.0 eq), $Ti(Oi\text{-}Pr)_4$ (1.5 eq), Et_2O, rt		(24)	375
		c-C_5H_9MgCl (4.0 eq), $Ti(Oi\text{-}Pr)_4$ (1.5 eq), Et_2O or PhMe, rt		(33)	375

TABLE 7. INTRAMOLECULAR CYCLOPROPANATION OF UNSATURATED CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

	Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}		c-C_5H_9MgCl (4.5 eq), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 **I** +  **II** **I** + **II** (78), dr 74:26	376
C_{24}		c-C_5H_9MgCl (3–4.5 eq), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 (52)	81
		c-$C_6H_{11}MgBr$ (5 eq), $MeTi(Oi$-$Pr)_3$ (1.5 eq), THF, 20°	 (43)	96
$C_{25–35}$	 R^1, R^2 = Et, Et; Ph, Me; Bn, Bn; PMP, Me	c-C_5H_9MgCl (4 eq), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 (80–95)	216
C_{25}		c-C_5H_9MgCl (4.0 eq), $Ti(Oi$-$Pr)_4$ (1.5 eq), THF, 20°	 (14)	375
C_{26}		c-$C_6H_{11}MgBr$ (5 eq), $MeTi(Oi$-$Pr)_3$ (1.5 eq), THF, rt	 (79)	377

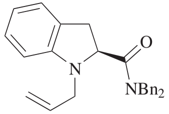
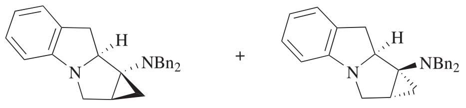
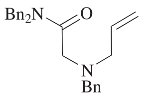
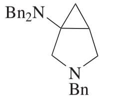
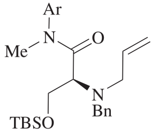
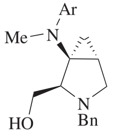
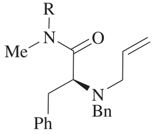
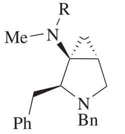
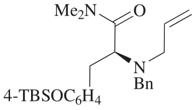
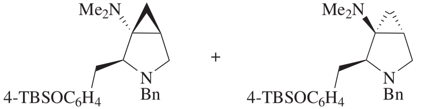
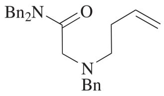
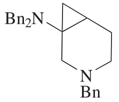
		c-$C_6H_{11}MgBr$ (5 eq), $MeTi(O$*i*-$Pr)_3$ (1.5 eq), THF, rt	 **I** **I + II** (61), dr 1:1 **II**	377
		c-$C_6H_{11}MgBr$ (5 eq), $MeTi(O$*i*-$Pr)_3$ (1.5 eq), THF, 20°	 (58)	96
C_{26-27}		1. c-C_5H_9MgCl (4.5 eq), $ClTi(O$*i*-$Pr)_3$ (1 eq), THF, rt 2. n-Bu_4NF	 Ar Ph (30) PMP (28)	378
C_{27}		c-C_5H_9MgCl (4.5 eq), $ClTi(O$*i*-$Pr)_3$ (1 eq), THF, rt	 R PMP (68) Bn (85)	378
		c-C_5H_9MgCl (4.5 eq), $ClTi(O$*i*-$Pr)_3$ (1 eq), THF, rt	 **I** **I + II** (87), dr 72:28 **II**	376
		c-$C_6H_{11}MgBr$ (4 eq), $MeTi(O$*i*-$Pr)_3$ (1.5 eq), THF, 20°	 (59)	96

TABLE 7. INTRAMOLECULAR CYCLOPROPANATION OF UNSATURATED CARBOXAMIDES WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

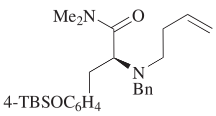
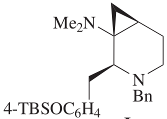
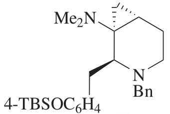
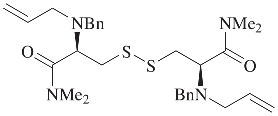
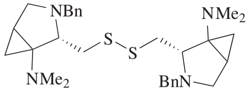
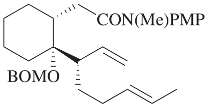
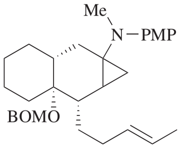
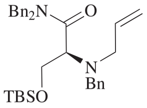
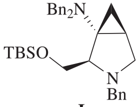
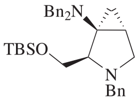
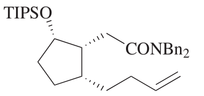
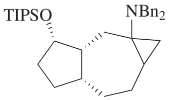
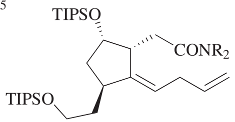
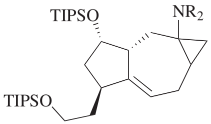
	Carboxamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}		c-C_5H_9MgCl (4.5 eq), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 **I** +  **II** **I** + **II** (37), dr 9:1	378
C_{30}		c-C_5H_9MgCl, $ClTi(Oi$-$Pr)_3$, THF, rt	 (40)	378
C_{32}		c-C_5H_9MgCl (3–4.5 eq), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 (>90)	216
C_{33}		c-$C_6H_{11}MgBr$ (4.6 eq), $MeTi(Oi$-$Pr)_3$ (1.4 eq), THF, 20°	 **I** +  **II** **I** + **II** (83), dr 2.5:1	96
C_{34}		c-C_5H_9MgCl (3–4.5 eq), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 (78)	81
$C_{35–45}$		c-C_5H_9MgCl (3–4.5 eq), $ClTi(Oi$-$Pr)_3$ (1 eq), THF, rt	 R Et (71) Bn (83)	81

TABLE 8. CYCLOPROPANATION OF NITRILES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES

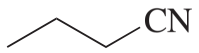
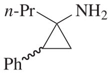
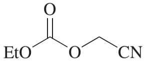
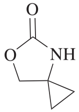
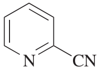
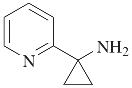
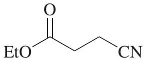
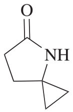
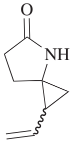
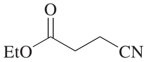
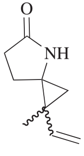
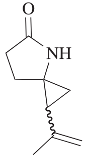
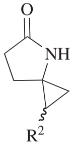
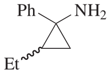
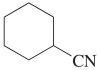
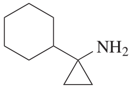
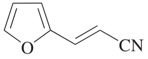
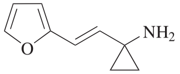
Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			
MeCN	Et_2Zn (1.2 eq), MeTi(O*i*-Pr)$_3$ (1–2 eq), LiO*i*-Pr (2.5 eq), LiI (2.5 eq), THF, rt	 (12)	94
C_4			
	1. Ph$(CH_2)_2$MgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	 (54) dr 68:32	91
C_5			
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et_2O, rt	 (31) +  (32)	93
C_6			
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, rt	 (57)	92
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (*x* eq), Et_2O, rt	 *x* 1.1 (80) 0.2 (73) 0.1 (68) 0.05 (29)	97, 93
	CH_2=CH$(CH_2)_2$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O or THF, 20°	 Solvent dr Et_2O (76) 5.5:1 THF (84) 14:1	379

TABLE 8. CYCLOPROPANATION OF NITRILES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	CH_2=C(Me)$(CH_2)_2$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O or THF, 20°	 **I** +  **II** Solvent **I** dr **II** dr Et_2O (40) 90:10 (21) 76:26 THF (44) >98:2 (24) 97:3	379
	R^1MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (*x* eq), Et_2O, rt	 R^1 *x* R^2 dr *n*-Bu 1.1 Et (74) 82:18 *n*-Bu 0.2 Et (76) 85:15 $Bn(CH_2)_2$ 0.2 Bn (59) 4:1	 93, 97 93, 97 93
C_7			
PhCN	Et_2Zn (2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), NaO*i*-Pr (2 eq), THF, rt	 (25)	94
	1. *n*-BuMgBr or *s*-BuMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	 (25)	380
	1. EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	 (52)	91
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (42)	380

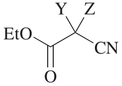
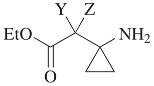
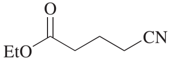
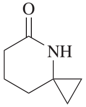
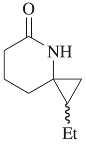
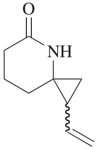
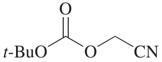
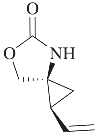
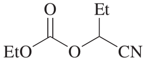
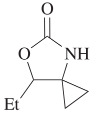
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)		Y Z —CH$_2$— (51) Me Me (35)	97
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (*x* eq), Et$_2$O, rt		*x* 1.1 (63) 0.2 (72)	97 93
	n-BuMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt		(50) dr 78:22	93
	CH$_2$=CH(CH$_2$)$_2$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O or THF, 20°		Solvent dr Et$_2$O (75) 70:30 THF (77) 63:37	379
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, 0°		(64)	93
	CH$_2$=CH(CH$_2$)$_2$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O or THF, 20°		(57)	379
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, 0°		(72)	97

TABLE 8. CYCLOPROPANATION OF NITRILES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Nitrile	Conditions	Product(s) and Yield(s) (%)			Refs.
C_{7-8}			Ar		
ArCN	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)		Ph	(65)	380
			4-FC$_6$H$_4$	(64)	
			3-ClC$_6$H$_4$	(72)	
			2-BrC$_6$H$_4$	(71)	
			3-BrC$_6$H$_4$	(76)	
			2-MeOC$_6$H$_4$	(58)	
			3-MeOC$_6$H$_4$	(73)	
			4-MeOC$_6$H$_4$	(43)	
			4-MeC$_6$H$_4$	(73)	
C_{7-11}			Ar		
	Et$_2$Zn (1.2 eq), MeTi(O*i*-Pr)$_3$ (1.2 eq), LiO*i*-Pr (2.5 eq), LiI (2.5 eq),THF, rt		2-Py	(80)	94
			3-Py	(82)	
			Ph	(62)	
			4-FC$_6$H$_4$	(65)	
			4-ClC$_6$H$_4$	(75)	
			4-BrC$_6$H$_4$	(72)	
			2-MeC$_6$H$_4$	(54)	
			3-MeC$_6$H$_4$	(53)	
			4-MeC$_6$H$_4$	(56)	
			3-CF$_3$C$_6$H$_4$	(73)	
			2-MeOC$_6$H$_4$	(47)	
			3-NCC$_6$H$_4$	(75)	
			2,4-(MeO)$_2$C$_6$H$_3$	(40)	
			3-*t*-BuO$_2$CC$_6$H$_4$	(73)	
			2-C$_{10}$H$_7$	(71)	

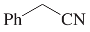
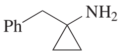
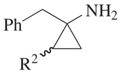
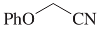
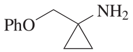
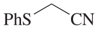
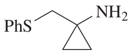
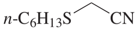
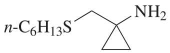
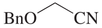
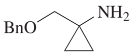
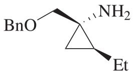
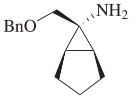
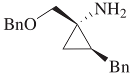
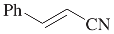
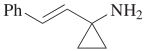
C_8			
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 **I** (70)	91
	Et$_2$Zn (1.2 eq), MeTi(O*i*-Pr)$_3$ (1–2 eq), LiO*i*-Pr (2.5 eq), LiI (2.5 eq), THF, rt	**I** (16)	94
	1. R^{1}MgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, rt 2. BF$_3$•OEt$_2$ (2 eq)	 R^1 / R^2 / dr *n*-Bu / Et / (57) / 64:36 *s*-Bu / Et / (54) / 55:45 PhCH$_2$CH$_2$ / Ph / (51) / 68:32	91
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, rt	 **I** (49)	92
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	**I** (80)	92
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, rt	 **I** (5)	92
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	**I** (39)	92

TABLE 8. CYCLOPROPANATION OF NITRILES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	EtMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 **I** (20)	92
	1. EtMgBr (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	**I** (54)	92
C_9 	EtMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 **I** (74)	92, 93
	1. EtMgBr (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	**I** (75)	92
	n-BuMgBr (2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 (61) dr 7:3	92
	c-C_5H_9MgCl (2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 (45) dr 86:14	92
	$Ph(CH_2)_3MgBr$ (2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 (64) dr 64:36	92
	1. EtMgBr (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (65)	380

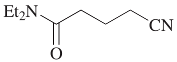
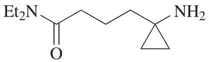
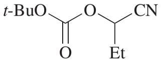
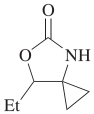
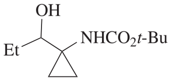
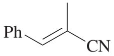
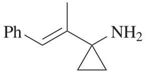
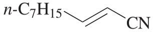
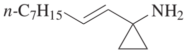
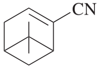
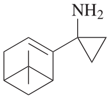
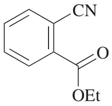
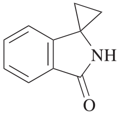
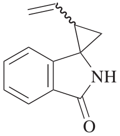
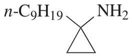
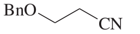
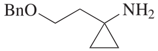
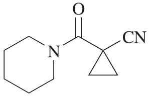
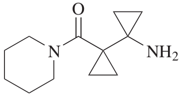
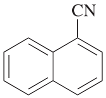
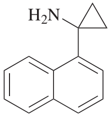
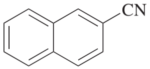
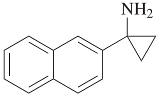
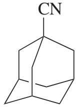
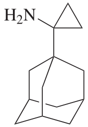
		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 (46)	97
		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (0.2 eq), Et$_2$O, rt	 (48) +  (12)	93
C_{10}		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 (46)	380
		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 (50)	380
		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 (62)	380
		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, rt	 (66)	380
		CH$_2$=CH(CH$_2$)$_2$MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O or THF, 20°	 Solvent dr Et$_2$O (85) 70:30 THF (81) 70:30	379

TABLE 8. CYCLOPROPANATION OF NITRILES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
n-$C_9H_{19}CN$	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (70)	91
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (54)	91, 92
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (40)	97
C_{11}			
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (57)	380
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (57)	380
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et_2O, –70° to rt 2. BF_3•OEt_2 (2 eq)	 (53)	91

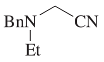
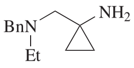
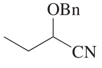
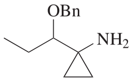
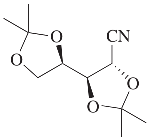
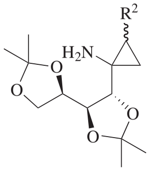
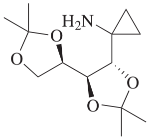
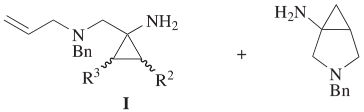
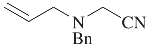
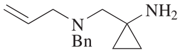
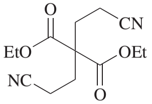
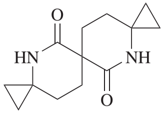
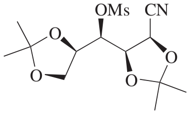
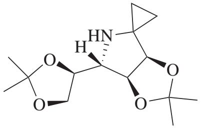
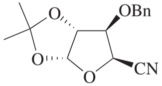
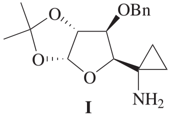
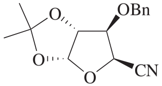
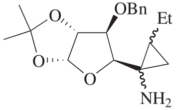
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, rt	 (64)	92
		n-BuMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, rt	 (72) dr 63:37	92
		EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, rt	 (73)	92
		R^{1}MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –78° to rt	 R^1 R^2 dr Et H (57) — *i*-Pr Me (59) 51:21:17:11 *n*-Bu Et (63) 45:22:22:11	381
		1. EtMgBr (1.5 eq), MeTi(O*i*-Pr)$_3$ (1.5 eq), THF, rt 2. BF$_3$•OEt$_2$ (2 eq)	 (80)	382
C$_{12}$		1. R^{1}MgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 **I** **II** R^1 R^2 R^3 **I + II** **I:II** *i*-Pr H Me (61) 78:22 *n*-Bu H Et (67) 84:16 *c*-C$_5$H$_9$ —(CH$_2$)$_3$— (60) 83:17	95

TABLE 8. CYCLOPROPANATION OF NITRILES WITH ALKOXYTITANACYCLOPROPANES GENERATED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES (*Continued*)

Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 (60)	95
C_{13}			
	EtMgBr (2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), THF, rt	 (60)	97
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq) 3. NaOH, H$_2$O	 (38)	383
	EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –78° to rt	 **I** (27)	381
	1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	**I** (54)	381
C_{15}			
	1. *n*-BuMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)	 (50) dr 40:26:22:12	381

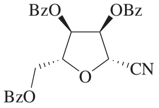
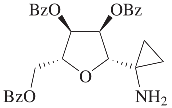
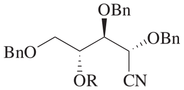
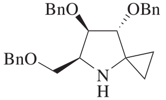
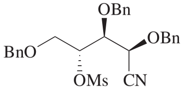
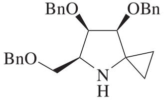
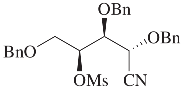
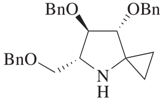
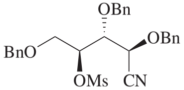
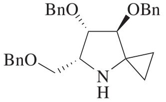
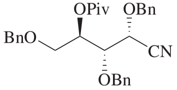
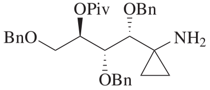
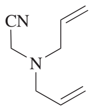
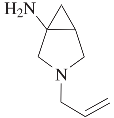
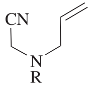
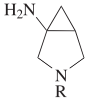
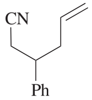
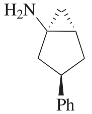
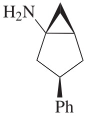
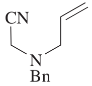
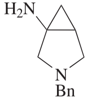
C_{27}		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq)		(55)	381
		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq) 3. NaOH, H$_2$O		R Ms (42) Ts (20)	383, 384
		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq) 3. NaOH, H$_2$O		(45)	383
		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq) 3. NaOH, H$_2$O		(40)	383
		1. EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –70° to rt 2. BF$_3$•OEt$_2$ (2 eq) 3. NaOH, H$_2$O		(40)	383
C_{31}		EtMgBr (2.2 eq), Ti(O*i*-Pr)$_4$ (1.1 eq), Et$_2$O, –78° to rt		(62)	381

TABLE 9. INTRAMOLECULAR CYCLOPROPANATION OF UNSATURATED NITRILES WITH ALKOXYTITANACYCLOPROPANES

Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 **I** (58)	95
	1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt 2. $BF_3•OEt_2$ (2 eq)	**I** (67)	95
$C_{10–12}$ 	1. c-$C_6H_{11}MgCl$ (2 eq), $MeTi(Oi\text{-}Pr)_3$ (1.1 eq), THF, 20° 2. Reagent (2 eq)	 R | Reagent | Temp (°) | Time (h) | Bn | $BF_3•OEt_2$ | 20 | 1 | (trace) Bn | $BF_3•OEt_2$ | 70 | 2 | (46) Bn | LiI | 70 | 3 | (48) Bn | LiI | 70 | 16 | (43) Bn | NaI | 70 | 3 | (28) Boc | LiI | 70 | 14 | (trace) Boc | LiI | 70 | 3 | (41)	96
C_{12} 	c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 **I** +  **II** **I** + **II** (58), **I**:**II** = 2:1	95
	1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt 2. $BF_3•OEt_2$ (2 eq)	**I** + **II** (62), **I**:**II** = 2:1	95
	c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 **I** (66)	95

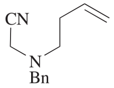
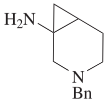
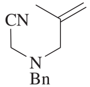
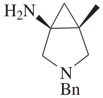
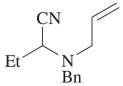
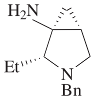
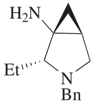
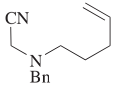
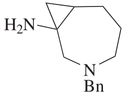
		c-$C_6H_{11}MgCl$ (3 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt	**I** (37)	95
		1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	**I** (69)	95
C_{13}		c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt	 **I** (11)	95
		1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	**I** (60)	95
		c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt	 **I** (62)	95
		1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	**I** (69)	95
C_{14}		c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt	 **I** +  **II** **I** + **II** (59), **I**:**II** = 2.6:1	95
		1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	**I** + **II** (67), **I**:**II** = 2.6:1	95
		1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(O$*i*$-Pr)_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	 (27)	95

TABLE 9. INTRAMOLECULAR CYCLOPROPANATION OF UNSATURATED NITRILES WITH ALKOXYTITANACYCLOPROPANES (*Continued*)

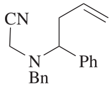
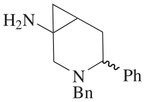
Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt	 **I** (36) dr 1:1	95
	1. c-$C_6H_{11}MgCl$ (2.2 eq), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 (2 eq)	**I** (62) dr 1:1	95

TABLE 10. CYCLOPROPANATION OF IMIDES WITH ALKOXYTITANACYCLOPROPANES

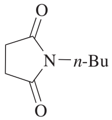
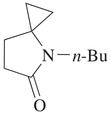
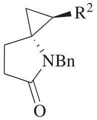
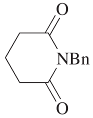
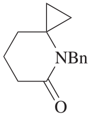
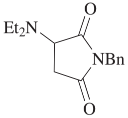
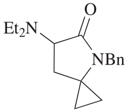
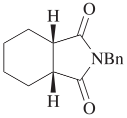
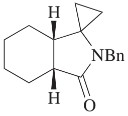
	Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		1. EtMgBr (1.5 eq), MeTi(O*i*-Pr)$_3$ (1.5 eq), THF 2. BF$_3$•Et$_2$O (2 eq)	 (74)	112
C_{11}		1. R^{1}MgBr (1.5 eq), MeTi(O*i*-Pr)$_3$ (1.5 eq), THF 2. BF$_3$•Et$_2$O (2 eq)	 R^1 R^2 dr Et H (74) — *n*-Bu Et (51) 68:32 Ph(CH$_2$)$_3$ Bn (48) 65:35	112
C_{12}		1. EtMgBr (1.5 eq), MeTi(O*i*-Pr)$_3$ (1.5 eq), THF 2. BF$_3$•Et$_2$O (2 eq)	 (67)	112
C_{15}		1. EtMgBr (1.5 eq), MeTi(O*i*-Pr)$_3$ (1.5 eq), THF 2. BF$_3$•Et$_2$O (2 eq)	 (58)	112
		1. EtMgBr (1.5 eq), MeTi(O*i*-Pr)$_3$ (1.5 eq), THF 2. BF$_3$•Et$_2$O (2 eq)	 (78)	112

TABLE 11. INTRAMOLECULAR CYCLOPROPANATION OF VINYL-TETHERED IMIDES WITH ALKOXYTITANACYCLOPROPANES

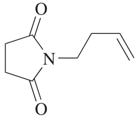
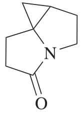
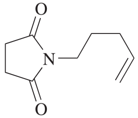
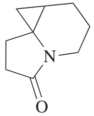
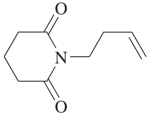
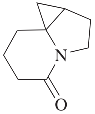
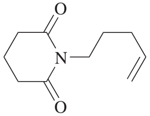
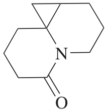
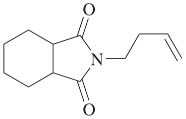
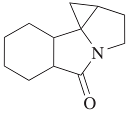
	Imide	Conditions	Product(s) and Yield(s) (%)		Refs.
C_8		1. c-$C_6H_{11}MgCl$ (2 eq), MeTi(Oi-Pr)$_3$ (2 eq), THF 2. BF_3•Et_2O (2 eq)		(65)	112
C_9		1. c-$C_6H_{11}MgCl$ (2 eq), MeTi(Oi-Pr)$_3$ (2 eq), THF 2. BF_3•Et_2O (2 eq)		(51)	112
		1. c-$C_6H_{11}MgCl$ (2 eq), MeTi(Oi-Pr)$_3$ (2 eq), THF 2. BF_3•Et_2O (2 eq)		(62)	112
C_{10}		1. c-$C_6H_{11}MgCl$ (2 eq), MeTi(Oi-Pr)$_3$ (2 eq), THF 2. BF_3•Et_2O (2 eq)		(46)	112
C_{12}		1. c-$C_6H_{11}MgCl$ (2 eq), MeTi(Oi-Pr)$_3$ (2 eq), THF 2. BF_3•Et_2O (2 eq)		(50)	112

TABLE 12. CYCLOPROPANATION OF SILYLKETENES WITH ALKOXYTITANACYCLOPROPANES DERIVED FROM GRIGNARD REAGENTS AND TITANIUM ALKOXIDES

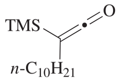
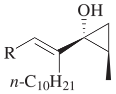
Silylketene	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	1. i-PrMgCl (2.75 eq), $Ti(Oi\text{-}Pr)_4$ (1.25 eq), Et_2O, –78 to –35° 2. RCHO (1.87 eq), –35°	 R Me (34) Et (33) 2-furyl (31) n-C_5H_{11} (42) Ph (25)	102

TABLE 13. CYCLOPROPANATION OF VINYLOGOUS ESTERS WITH ALKOXYTITANACYCLOPROPANES

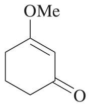
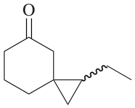
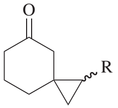
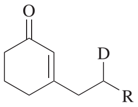
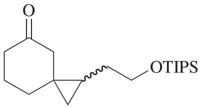
<table>
<tr><th>Carboxylic Ester</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C₇
</td><td>n-BuMgBr (excess),
Ti(Oi-Pr)$_4$ (1.1 eq),
PhMe, rt</td><td> (77) dr 2:1</td><td>98</td></tr>
<tr><td></td><td>1. RCH$_2$CH$_2$MgBr (excess),
Ti(Oi-Pr)$_4$ (1.1 eq),
Et$_2$O or THF, rt
2. D$_2$O</td><td> **I** dr 2:1 +  **II**
<table>
<tr><th>R</th><th>Solvent</th><th>I</th><th>II</th></tr>
<tr><td>H</td><td>Et$_2$O</td><td>(46)</td><td>(0)</td></tr>
<tr><td>Et</td><td>Et$_2$O</td><td>(77)</td><td>(0)</td></tr>
<tr><td>Et</td><td>THF</td><td>(0)</td><td>(49)</td></tr>
<tr><td>i-Pr</td><td>Et$_2$O</td><td>(54)</td><td>(0)</td></tr>
<tr><td>Ph</td><td>Et$_2$O</td><td>(43)</td><td>(0)</td></tr>
<tr><td>TIPSO(CH$_2$)$_2$</td><td>Et$_2$O</td><td>(45)</td><td>(7)</td></tr>
<tr><td>TIPSO(CH$_2$)$_2$</td><td>THF, Et$_2$O</td><td>(5)</td><td>(42)</td></tr>
</table></td><td>98</td></tr>
<tr><td></td><td>1. TIPSO(CH$_2$)$_4$MgBr (excess),
Ti(Oi-Pr)$_4$ (1.1 eq),
Et$_2$O or THF, rt
2. BF$_3$•OEt$_2$</td><td> (50)</td><td>98</td></tr>
</table>

TABLE 14. CYCLOPROPANATION OF VINYLOGOUS ESTERS WITH ALKOXYTITANACYCLOPROPANES GENERATED BY LIGAND EXCHANGE

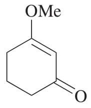
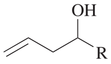
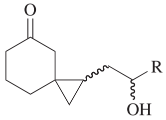
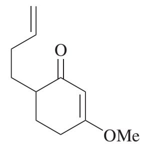
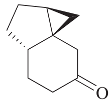
Carboxylic Ester	Olefin	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		c-C_5H_9MgCl (excess), Ti(Oi-Pr)$_4$ (1.1 eq), Et_2O, rt	 R H (45) Bn (52)	98

TABLE 15. INTRAMOLECULAR CYCLOPROPANATION OF VINYLOGOUS ESTERS WITH ALKOXYTITANACYCLOPROPANES

Carboxylic Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	1. c-C_5H_9MgCl (excess), $Ti(Oi\text{-}Pr)_4$ (1.1 eq), Et_2O, rt 2. BF_3•OEt_2 3. TsOH, H_2O	 (80)	98

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CHAPTER 2

THE BARTON-McCOMBIE REACTION

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CONTENTS

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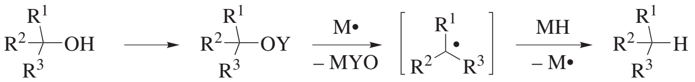
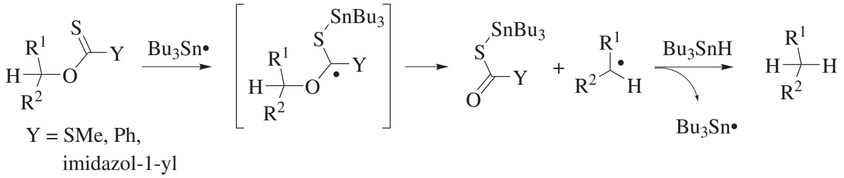
INTRODUCTION

Deoxygenations of alcohols, i.e. processes that replace a hydroxyl group with hydrogen at a saturated carbon, find applications in both total synthesis and the systematic modification of natural products. They may also be employed to introduce deuterium or tritium in a site-specific manner. Reductive methods that involve ionic or highly polarized reagents or intermediates can be limited in their applicability: for example, competing reaction pathways including cationic rearrangements and anionic eliminations may be encountered in sterically hindered systems and with substrates bearing heteroatoms close to the center undergoing reduction. As evidenced by developments over the last few decades, methods that involve the generation and direct quenching via hydrogen atom abstraction of the derived, carbon-centered radical typically show the greatest tolerance for the presence of other functional groups and for variations in both the steric and the electronic environment in the vicinity of the center undergoing deoxygenation. Since derivatization of the hydroxyl is a prerequisite, Eq. 1 represents the process in general form. The determinant factors for efficient formation of the deoxygenated product lie in the ability of the combination of M• and Y to induce homolysis of the C−O bond, coupled with the ability of MH to rapidly reduce the radical R• by hydrogen donation, thereby propagating an efficient chain process.



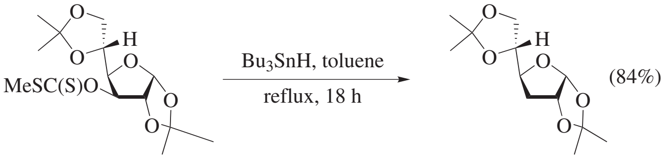
(Eq. 1)

A high-yielding way to realize this sequence was first described by Barton and McCombie[1] using the free-radical chain reaction of *O*-thioacyl derivatives of secondary alcohols with tri-*n*-butylstannane (Bu_3SnH), as shown in Scheme 1.



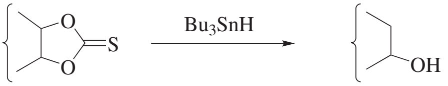
Scheme 1

A typical deoxygenation of an *O*-(methylthiothiocarbonyl) derivative (an *S*-methyl xanthate) of a secondary alcohol is shown in Eq. 2.[1]

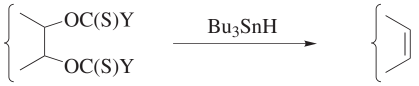


(Eq. 2)

Since the initial discovery, variations in the nature of the thiocarbonyl substituent (Y) and the propagating radical/*H*-donor combination have provided options for fine-tuning both the derivatization and reduction steps. These modifications have extended this chemistry to: (1) thioacyl derivatives of primary and tertiary alcohols; (2) the reduction of cyclic thiocarbonates of diols to monodeoxygenated products (Eq. 3); and (3) the conversion of 1,2-bis(*O*-thioacyl) compounds into the corresponding olefins (Eq. 4).



(Eq. 3)



(Eq. 4)

This chapter provides a detailed description and comparison of the combinations of substrates (ROC(S)Y) and reagents (MH) that will bring about these processes, and also provides a summary and evaluation of alternative deoxygenation methods. The "Tabular Survey" includes all primary, secondary, and tertiary alcohol deoxygenations, reductions of cyclic thiocarbonates, and olefin formations from bis(*O*-thioacyl) derivatives of 1,2-diols.

Free-radical deoxygenations and related processes have been previously reviewed, both specifically[2] and within articles on the free-radical chemistry of thiocarbonyl compounds,[3–5] free-radical reactions in natural product and carbohydrate chemistry,[6–8] free-radical reactions in general,[9] reductive processes for C–O and C–N bonds,[10] the organic chemistry of tin hydrides,[11,12] and tin hydride substitutes in radical reactions.[13]

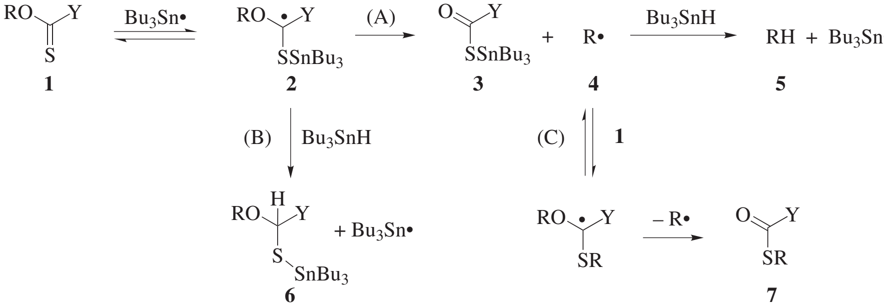
The following sections discuss mechanistic and stereochemical issues, set out the scope and limitations of these processes with respect to both the thioacylation and reduction steps, and exemplify some applications to both total synthesis and the modification of natural products. Comparisons are made with alternative free-radical methods, with hydrogenolytic methods, and with deoxygenation processes involving ionic or highly polarized reagents or intermediates. Consideration is also given to general experimental conditions, including issues of handling, toxicity, and product isolation associated with the reagents involved in the reaction. The "Tabular Survey" shows the deoxygenation step; options and conditions for the *O*-thioacylation step are discussed in detail in the "Scope and Limitations" section and are included in the "Experimental Procedures," but are not included in the tables. The literature is covered through the end of 2007 in Tables 1–5; examples appearing in 2008 through mid-2009 are in the Supplemental Tables 6A-6K. Every effort has been made to find all of the applications of this method for inclusion in the tables; however, given the vastness of the literature, some accidental omissions are likely and are regretted by the authors.

MECHANISM AND STEREOCHEMISTRY

Mechanism

Reductions of *O*-Thioacyl Derivatives with Bu_3SnH. On the basis of the experimental results outlined below, Scheme 2 shows the major mechanistic steps in the radical chain reduction of an *O*-thioacyl compound **1** with Bu_3SnH to afford the deoxygenated compound **5** and known byproducts encountered in such reactions. This Scheme expands the initial proposal[1] by the addition of reversibility in the step that forms the stabilized radical **2** and the alternative capture of the radical **4** by the starting thiocarbonyl compound.

Following the formation of adduct radical **2**, fragmentation, energetically driven by the formation of a carbonyl group (path A), leads largely to the deoxy product **5**. Path C, involving radical capture by the starting material and leading to the isomeric thiol ester **7**, is usually a minor contributor when an efficient *H*-donor such as Bu_3SnH is employed. Co-product **3** may undergo other transformations, as discussed below. However, some of radical **2** may be directly reduced to afford adduct **6** (path B), the amount of which depends on both the reaction conditions and the structure of the substrate. The delicate balance between the

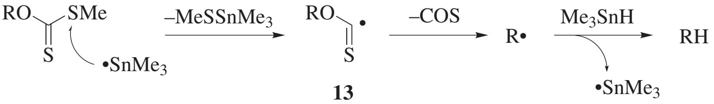


Scheme 2

desired fragmentation and the undesired conversion into adduct **6** is most significant when R is primary. The practical consequences of this balance for all substrates with regard to selecting the reducing agent, conditions, and the group Y are discussed in the "Scope and Limitations" section. The ultimate products formed from **6** are derived either from hydrolysis upon workup or from further reduction. Thus, in addition to the desired deoxygenated product, identified products from ROC(S)Y reductions, when Y is a heteroatom, include the alcohol **8**, the further reduction product **9** or its initial hydrolysis product **10**,[1] and the methyl ether **11**.[14] From *O*-thiobenzoates (Y = Ph), the alcohol **8** and the benzyl ether **12** may be obtained.[15] Similar conversions of the thiocarbonyl group into a methylene group are also encountered in reductions of cyclic thiocarbonates.

ROH	$ROCH_2SSnBu_3$	$ROCH_2SH$	$ROCH_3$	$ROCH_2Ph$
8	**9**	**10**	**11**	**12**

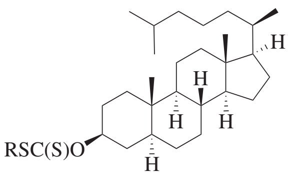
The photolysis of an *S*-methyl xanthate with hexamethyldistannane at −20° allows the observation (ESR) of alkoxythiocarbonyl radicals **13** and suggests an alternative mechanism for these reductions, involving direct, homolytic displacement (S_H2) on the methylthio group (Scheme 3).[16]



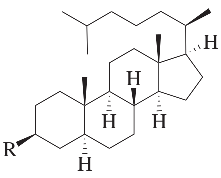
Scheme 3

Although the loss of carbonyl sulfide (COS) from **13** is known to be a facile process when such species are generated unambiguously,[17,18] competition experiments suggest that Scheme 3 represents, at most, a minor process under typical reduction conditions.[19,20] When xanthates derived from 5α-cholestan-3β-ol are reduced at 80°, with initiation by AIBN [2,2′-azobis(2-cyanopropane)], the *S*-isopropyl compound **14** is much more reactive than the *S*-methyl compound **15**, a result inconsistent on steric grounds with the S_H2 mechanism but consistent with facile, reversible addition of Bu_3Sn• to the thiocarbonyl group of both xanthates, with preferential fragmentation of the more crowded adduct radical derived from **14**. This attack is followed by scission of the secondary S−*i*-Pr bond rather than the C−O bond to give the stannyl xanthate **16**. With excess Bu_3SnH, the latter is reduced to the deoxygenated compound **19**.

Product ratios also provide mechanistic information: with 2 equivalents of Bu_3SnH at 110°, both **15** and the two *S*-aryl xanthates **17** and **18** are reduced efficiently to 5α-cholestane (**19**) whereas at 80° the yield of **19** is somewhat lower, and significantly differing amounts of the *S*-(tri-*n*-butylstannyl) hemithioacetal **20** are produced from the different xanthates. If the alkoxythiocarbonyl radical is the common intermediate, the same ratio of **19**:**20** is expected from each xanthate. Hemithioacetal **20** is formed from intermediate **6** (Scheme 2, Y = SR) either by



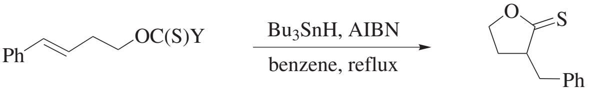
	R
14	*i*-Pr
15	Me
16	Bu_3Sn
17	Ph
18	2,4,6-$Me_3C_6H_2$



	R
19	H
20	OCH_2SSnBu_3
21	OC(S)H

direct reduction by selective, S_H2 attack of Bu_3Sn• at the methylthio group, or by extrusion of Bu_3SnSR to afford the *O*-thioformate **21**, which is known to be rapidly reduced to **20**. A similar extrusion of Bu_3SnSMe from the adduct radical (**2**, Scheme 2, Y = SMe) is an alternative and likely route to any ROCS• formed in these reactions.[5]

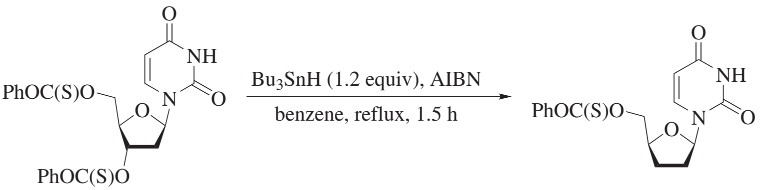
The initially formed radical (**2** in Scheme 1, on the basis of the studies described above) in these deoxygenations can be trapped before fragmentation by a suitably disposed, activated olefin (Eq. 5),[21] acetylene,[22] or hydrazone.[23] Such cyclization results, taken alone, do not securely distinguish between **2** and **13** as the intermediate when the precursor is a xanthate.[24]



Y	Yield (%)
SMe	77
Im	70

(Eq. 5)

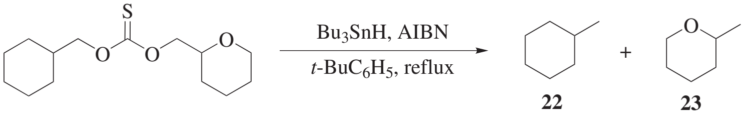
^{119}Sn NMR spectroscopic studies of Bu_3SnH reductions of *O*-cyclododecyl-*S*-methyl xanthate below room temperature (initiated by Et_3B-O_2) confirm that the initially formed co-product is $Bu_3SnSC(O)SMe$, which loses COS on gentle warming. *O*-(Phenoxythiocarbonyl) compounds behave similarly.[25] The reversible formation of **2** as the major pathway is also consistent with the observed selective reduction of a substrate with both primary and secondary sites, using limited amounts of the reducing agent (Eq. 6).[26] Reductions of ROC(S)Im species (Im = imidazol-1-yl) with Bu_3SnH also produce COS, plus 1-(tri-*n*-butylstannyl)imidazole (Bu_3SnIm) as the co-product.[1,27]



(63%)

(Eq. 6)

Although initial observations suggested otherwise,[28] other studies[29,30] establish that electronic effects from nearby (non-conjugated) substituents, notably alkoxy groups that are β to the radical center, do not significantly influence the ease of fragmentation, as shown by the relative amounts of products **22** and **23** in (Eq. 7).[30]



22 **23**

22:**23** = 1.76:1

(Eq. 7)

However, steric compression around the center undergoing reduction does facilitate C–O scission, and polar effects influence the rate of the propagation step, MH + R•. Electron-withdrawing groups in the vicinity of the radical center increase the propagation rate with electron-rich MH species,[31,32] accounting for the more rapid reduction of carbohydrate derivatives compared with hydrocarbon-like substrates.[33] The influence of polarization effects is elegantly demonstrated by the observation that a 1-(perfluoroalkyl)-substituted radical will readily abstract a hydrogen atom from cyclohexane, whereas its hydrocarbon counterpart will not.[31]

In general, deoxygenations using Bu$_3$SnH tend to be slower and can produce larger amounts of byproducts when conducted under rigorously oxygen-free conditions and in the absence of deliberately added free-radical initiators than similar deoxygenations exposed to oxygen or initiators. For less efficient *H*-donors, initiators are essential for successful reactions. It is not known whether mechanistic processes different from the above are involved; the possibility of electron transfer has been suggested.[34] However, the byproducts are different in proportion, not character, and no conversion is seen when radical inhibitors are included.

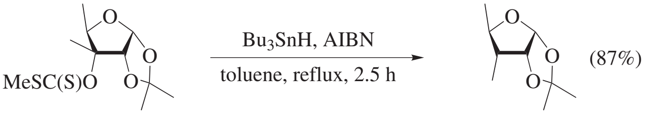
Reductions of *O*-Thioacyl Derivatives with Other *H*-Donors. Limited mechanistic information is available for other *H*-donor systems. In reductions using diphenylsilane, co-products analogous to those seen in Bu$_3$SnH reductions are observed.[35] In a reduction of a cyclic thiocarbonate with triphenylsilane (Ph$_3$SiH), the initially formed intermediate is apparently more thermally stable, since the bis(deoxy) product is obtained when excess Ph$_3$SiH is used. This result requires that the initially formed ROC(O)SSiPh$_3$ species is reduced via S$_H$2 attack at sulfur before it loses COS to form ROSiPh$_3$.[36] A similarly stable intermediate accounts for the high yield of deoxy nucleosides obtained in reactions of symmetrical thiocarbonates with Ph$_3$SiH.[37]

When the M–H bond strength in the *H*-donor is significantly higher than that in Bu$_3$SnH, the mechanistic picture can be more complicated. Radicals derived from the initiating system (which is needed in larger amounts to compensate for shorter chain lengths) may become the dominant species that add to the thiocarbonyl group, complicating the overall mechanistic picture. For example, in the system where the O–H in $R_3B{\bullet}H_2O$ is the donor,[38] reduction of a *sec*-ROC(S)SMe substrate with $Bu_3B–H_2O–O_2$ affords BuSC(O)SMe as the co-product. In addition, other species present in deoxygenation reactions may act as the *H*-donor. For example, the reduction of *cyclo*-$C_{12}H_{23}OC(S)NHPh$ to *cyclo*-$C_{12}H_{23}D$ using different M–D species gives deuterium incorporations ranging from 18% to 98%,[39] reflecting competition for the cyclododecyl radical between the deuteriated donor and the NH in the starting material or a co-product. In a system that is effective for reducing carbohydrate and cyclitol derivatives, stoichiometric amounts of lauroyl peroxide provide 1-undecyl radicals for addition to the thiocarbonyl group and the tertiary C–H of 2-propanol provides the hydrogen for the quenching step.[32]

Stereochemistry

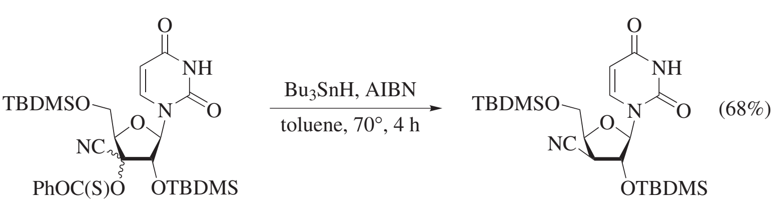
The reduction of a derivative of an unsymmetrical tertiary alcohol, or of a derivative of an appropriately substituted secondary alcohol using a deuteriated donor, can generate two stereoisomers. For the systems studied, the results indicate that steric hindrance of the approach of the *H*-donor to the carbon-centered radical dominates the stereochemical course of reduction. Contributions from electronic effects are relatively minor, except when they affect the conformation of the intermediate radical.

Tertiary Alcohol Derivatives. In the example shown in Eq. 8, the adjacent isopropylidene moiety directs the approach of the reducing agent to the carbon center undergoing reduction.[40]



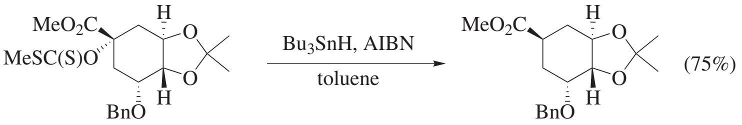
(Eq. 8)

The stereochemical course of a similar reduction at a tertiary center in a nucleoside is controlled by the orientation of the base (Eq. 9).[41]



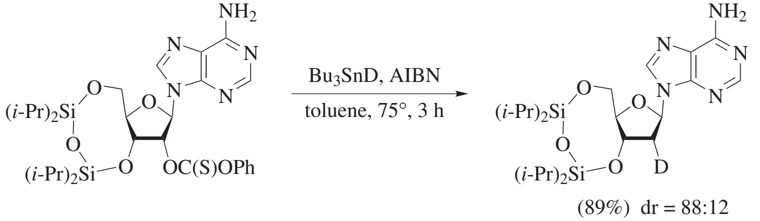
(Eq. 9)

For six-membered rings, the ability of the radical to adopt different conformations makes stereochemical outcomes less predictable. Secondary radicals at the anomeric position in hexopyranose derivatives undergo attack by olefins to form C–C bonds from the axial direction;[42] the corresponding reduction of an anomeric, tertiary radical by Bu_3SnH is less selective, although axial attack by Bu_3SnH still dominates.[43] Axial attack is also seen in a cyclitol (Eq 10).[44]



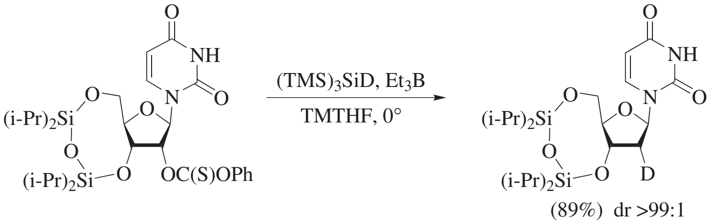
(Eq. 10)

Secondary Alcohol Derivatives. *O*-Thioacyl derivatives at C2 and C3 of the ribose moiety in nucleosides are reduced by Bu_3SnD with preferential delivery of deuterium *anti* to the base, typically with selectivity in the 80–90:20–10 range under the usual conditions (Eq. 11).[34]



(Eq. 11)

At lower temperatures, using tris(trimethylsilyl)silane-d [$(TMS)_3SiD$] in 2,2,5,5-tetramethyltetrahydrofuran (TMTHF), very high selectivity is obtained (Eq. 12).[45]



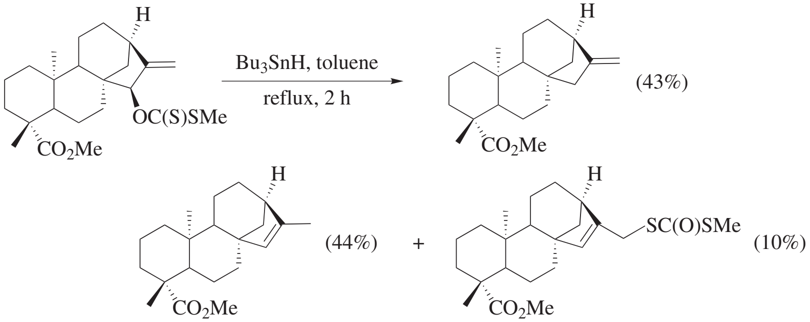
(Eq. 12)

Similar facial preferences are seen in reductions by Bu_3SnD of *S*-methyl xanthates derived from furanosides.[39,46,47] In reductions of fluorinated nucleoside derivatives[48] the product ratios are influenced by the presence of a fluorine substituent β to the radical, but capture of deuterium from the face *anti* to the base still dominates the outcome. In simpler systems, pyramidalization of a carbon-centered radical *anti* to an adjacent C–F bond has been suggested to account for stereochemical preferences in reductions of 2-bromofluoro compounds using Bu_3SnD.[49]

Site Selectivity

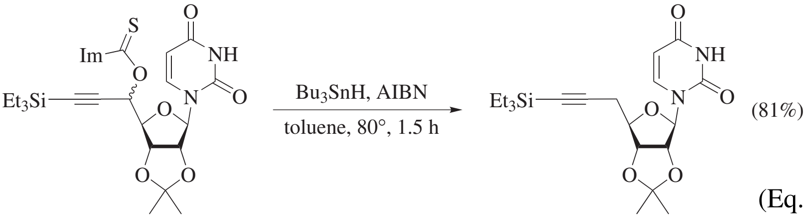
Reductions of *S*-methyl xanthates of allylic alcohols may be complicated by the formation of constitutional isomers in the hydrogen-capture step and also by competing, thermal isomerization of the starting material to the thiolcarbonate

(Eq. 13).[50] *O*-(Phenoxythiocarbonyl) derivatives of allylic alcohols rearrange at room temperature.[51]



(Eq. 13)

Reductions of *O*-thioacyl derivatives of propargylic alcohols take place without allene formation (Eq. 14).[52]



(Eq. 14)

The site selectivity of reductions of cyclic thiocarbonates is discussed in a later section.

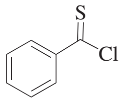
SCOPE AND LIMITATIONS

The Thioacylation Step

This section is subdivided according to alcohol structural type. Thioacylations of primary and secondary alcohols are grouped together and within this largest sub-section, methods for introducing all of the alternative thioacyl groups are described. Specific aspects of thioacylation of tertiary alcohols and diols are discussed in separate subsections.

Primary and Secondary Alcohols.

O-Alkyl Thioesters. Several methods are available for the preparation of these substrates. Within this class, thiobenzoates (ROC(S)Ph) are suitable for all secondary alcohol deoxygenations, and thioformates (ROC(S)H) find special applications to hindered substrates. For thiobenzoylations, the use of thiobenzoyl chloride (**24**) in pyridine is limited to unhindered alcohols and by the problems involved in preparing and storing the pure reagent.[53]



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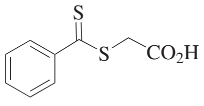

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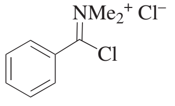

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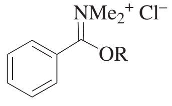
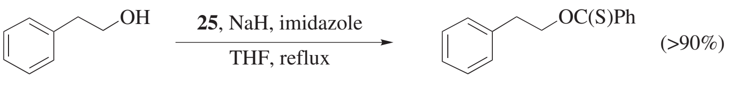


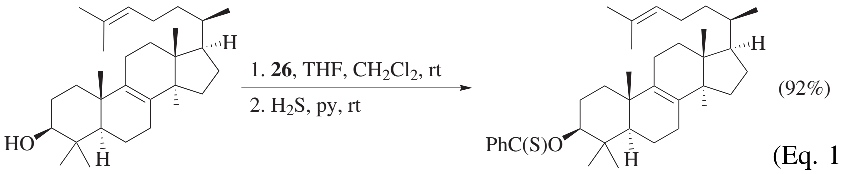
27

For substrates that are stable to relatively strong bases, a superior method involves the reaction of the alcohol with the stable, crystalline reagent **25** and sodium imidazolide. Yields are generally good, as the example in Eq. 15 shows,[53] but can be low for hindered systems.[1]



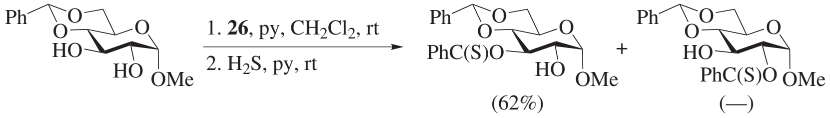
(Eq. 15)

A convenient and general method,[54] modified to avoid the use of an excess of the alcohol,[1] employs the α-chloroiminium salt **26**, which is prepared from *N*,*N*-dimethylbenzamide by reaction with phosgene or oxalyl chloride. Reaction of **26** with the alcohol, optionally in the presence of pyridine, forms the intermediate **27**, which is converted without isolation into the desired *O*-thioester with hydrogen sulfide-pyridine. Treatment of the same intermediate with buffered, ethanolic sodium hydroselenide produces the corresponding *O*-selenobenzoate; with sodium hydrotelluride, complete reduction to afford the benzyl ether is observed.[1] This protocol is applicable to hindered alcohols, as illustrated by the preparation of *O*-thiobenzoyl lanosterol (Eq. 16).[1]



(Eq. 16)

One advantage of the iminium salt method is that diols are converted only into mono-thiobenzoates, because the intermediate, charged species **27** is reluctant to react at an additional site with the similarly charged reagent **26**. In the example shown in Eq. 17,[1] the major product is the 3-isomer, whereas most other mono functionalizations (e.g., tosylation) of this substrate are selective for the C2 hydroxyl group.

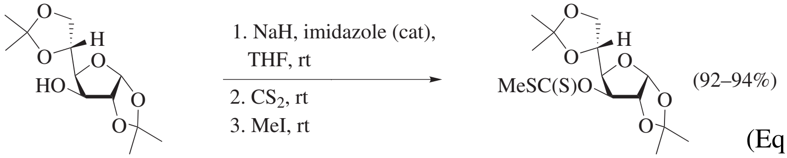


(Eq. 17)

Aryl-ring substituted thiobenzoates and aliphatic *O*-thioesters are similarly prepared. An analogous sequence using the parent Vilsmeier reagent

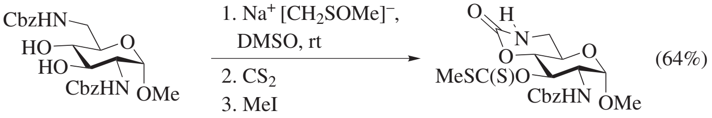
($ClCH{=}NMe_2^+\ Cl^-$) forms *O*-thioformates.[1] Activation of the amide by trifluoromethanesulfonic anhydride has also been used.[55] When an alcohol is too hindered to react with **26**, the thioformate can usually be prepared and deoxygenated. Limitations to this method arise when the alkoxyiminium species **27** decomposes very rapidly to produce either a chloro compound or an alkene. This is frequently the case for tertiary alcohols and allylic or benzylic alcohols, unless electron-withdrawing groups are nearby.

O-(Alkylthio- and Arylthiothiocarbonyl) Derivatives. Xanthates ($R^1OC(S)SR^2$) have a long history and exhibit rich free-radical chemistry.[4,5] The *S*-methyl compounds are frequently employed substrates for deoxygenation reactions. They are readily obtained by sequential treatment of the alcohol with base followed by carbon disulfide (CS_2) and finally iodomethane or dimethyl sulfate. A variety of bases may be employed, providing that they are capable of generating the alkoxide. Sodium hydride (NaH) is by far the most frequently used base, with tetrahydrofuran (THF) as the solvent. When the biphasic reaction between NaH and the alcohol is slow, a catalytic amount of imidazole serves as a convenient "proton shuttle."[1] Because the reaction of CS_2 with sodium alkoxides is rapid, it seems likely that any difficulty in forming a xanthate lies in the deprotonation step (see later, for tertiary alcohols). A typical *S*-methyl xanthate preparation is shown in Eq. 18.[56]



(Eq. 18)

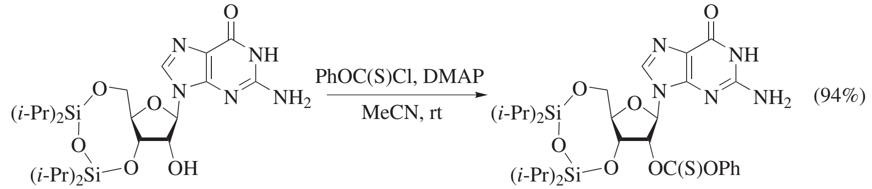
Migration of the protecting group during the preparation of a xanthate from a mono-*O*-TBS-1,2-diol is known,[57] and an analogous ester migration is avoided in one instance by operating at low temperatures.[58] The cyclic amidine 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) is also a suitable base[59,60] and can allow selective xanthate formation from a primary alcohol in the presence of a secondary alcohol.[59] When rapid deprotonation of the alcohol at or below room temperature is desirable, *n*-butyllithium, sodium bis(trimethylsilyl)amide, or potassium hydride can be employed. All of these reactions can be carried out in any aprotic solvent that is tolerant of the base and the alkoxide. In amino sugar derivatives containing carbamate-protected primary amine residues, sodium hydroxide in dimethyl sulfoxide (DMSO) has proven to be a useful base-solvent combination.[61] With anhydrous strong bases, the formation of a cyclic carbamate can precede the *O*-thioacylation step when an appropriately disposed *N*-benzyloxycarbonyl group is present (Eq. 19).[61]



(Eq. 19)

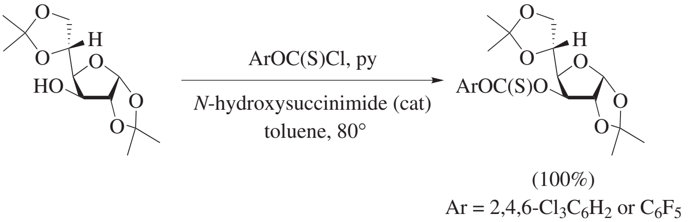
Phase-transfer conditions have been employed to obtain *S*-methyl xanthates from carbohydrate derivatives.[62] Other *S*-alkyl or *S*-arylmethyl xanthates such as the *S*-benzyl compounds[63] are obtained under any of the foregoing conditions, replacing the iodomethane with the appropriate alkylating agent. A Mitsunobu protocol for the preparation of aliphatic xanthates has also been reported.[64] The analogous *S*-aryl derivatives are prepared in three ways: by direct thioacylation with ArSC(S)Cl-pyridine;[61,65] by reacting the alcohol with thiophosgene and base, followed by the thiol;[65] or by treating the corresponding *O*-(imidazol-1-ylthiocarbonyl) derivative (ROC(S)Im) with the aryl thiol and base.[19]

O-(Aryloxy- and Alkoxythiocarbonyl) Derivatives. Introduced by Robins, *O*-phenoxythiocarbonyl (PTC) derivatives are versatile substrates for deoxygenations and have found application to diverse systems. The original publications[34,66] defined conditions that have proven to be general. For unhindered alcohols such as cholesterol, reaction with phenoxythiocarbonyl chloride (PTC-Cl) and pyridine (usually in dichloromethane) is recommended, whereas for more hindered systems reaction with PTC-Cl and 4-(dimethylamino)pyridine (DMAP) in acetonitrile is employed (Eq. 20).[34]



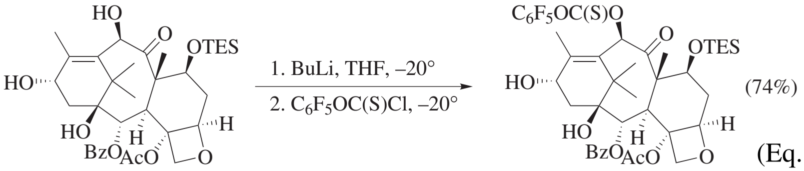
(Eq. 20)

Although Et_3N is not a suitable base because of amine dealkylation, a recent study[67] demonstrates that selective thioacylation of polyols with PTC-Cl is achieved using 1,2,2,6,6-pentamethylpiperidine as the stoichiometric base in the presence of sub-stoichiometric amounts of both iron(III) chloride and *N*-methylimidazole (NMI). By replacing NMI with a peptide bearing a terminal *N*-methylhistidine residue, useful changes in acylation selectivities are obtained. When a PTC or similar derivative is adjacent to a suitably disposed hydroxyl group, cyclization to a thiocarbonate can take place under thermal deoxygenation conditions, so it is advisable to protect such groups by acylation or silylation. Analogs of PTC derivatives with electron-withdrawing groups on the aryl ring are readily prepared by treating the alcohol with the appropriate aryloxythiocarbonyl chloride and pyridine in the presence of *N*-hydroxysuccinimide, as shown in Eq. 21.[68] As expected, $C_6F_5OC(S)Cl$ thioacylates cholesterol much faster than does the parent phenyl compound.[69] These and related derivatives are also obtained by reacting the alcohol with thiophosgene and base, followed by the phenol.[65]



(Eq. 21)

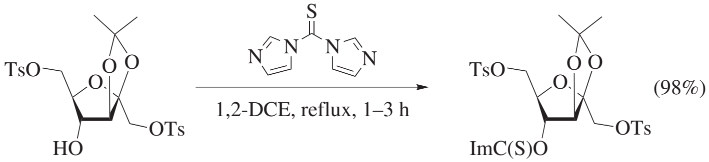
In a more complex system, selective deprotonation of the most acidic hydroxyl group followed by thioacylation has also been used with the pentafluorophenyl reagent (Eq. 22).[70]



(Eq. 22)

O-(Alkoxythiocarbonyl) derivatives are rarely employed as deoxygenation substrates. In nucleosides, the *O*-methyl derivatives are prepared by heating the corresponding *O*-(imidazol-1-ylthiocarbonyl) compounds (next section) with methanol,[71] and the symmetrical analogs are prepared using thiophosgene and DMAP.[37]

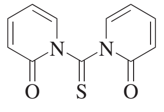
O-(Imidazol-1-ylthiocarbonyl) Derivatives and Related Substrates. Derivatives of the type ROC(S)Im are widely employed substrates in the deoxygenation reaction. These substances react with strong nucleophiles (thiolates, alkoxides, and aliphatic amines), but they are stable to water and alcohols at ambient temperature, and to silica gel. They are prepared[1] by heating the alcohol with 1.5–2 equivalents of 1,1′-thiocarbonyl diimidazole (Im_2CS, TCDI) in non-hydroxylic solvents. A typical preparation is shown in Eq. 23.[72]



(Eq. 23)

When the targeted hydroxyl group is located at a site where carbenium ion formation is particularly facile, the net result of treatment with TCDI can be replacement of the hydroxyl by the imidazol-1-yl group.[73]

The structurally related *O*-(2-oxo-1,2-dihydropyridin-1-ylthiocarbonyl) derivatives[74] appear to be equivalent to the foregoing imidazole derivatives, but have received less attention in terms of applications beyond the original examples. The reagent **28**, prepared by DMAP-catalyzed rearrangement of **29**, reacts with alcohols in refluxing toluene to afford high yields of the desired substrates; adduct **30** is a typical example. The subsequent reductive step is then carried out without isolating **30**; the co-product in the first step, 2-pyridinone, does not interfere with the reduction.



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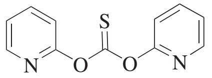

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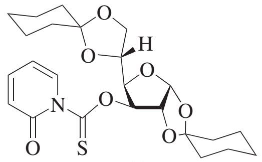

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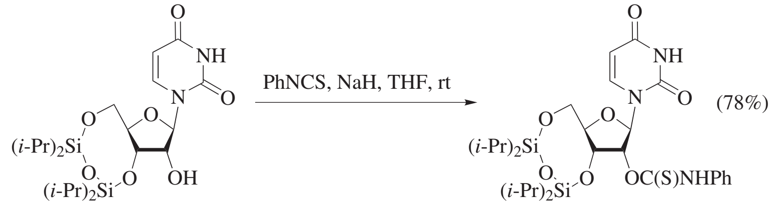
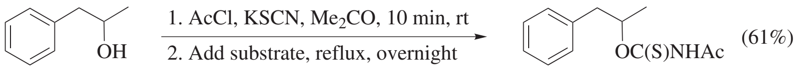
The potential advantages of this process lie in the greater air- and moisture-stability of **28** relative to TCDI, the non-basic character of the co-product, and the "one pot" nature of the overall conversion of ROH into RH. With both TCDI and **28**, 1,2- and 1,3-diols form cyclic thiocarbonates, unless this is not sterically feasible.

O-Thiocarbamoyl Derivatives and Related Substrates. Studies by the Nishiyama group[39,75–77] have added diverse *O*-thiocarbamates to the repertoire of deoxygenation substrates. From a preparative viewpoint the most convenient of these substrates would seem to be the *N*-phenyl compounds, which are obtained in yields ranging from 75–99% by treating the alcohol with NaH in the presence of phenyl isothiocyanate (Eq. 24).[39]



(Eq. 24)

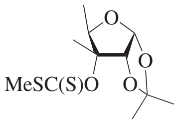
This modification is an improvement of an earlier method, which requires the conversion of the alcohol into the corresponding tri-*n*-butylstannyl ether prior to reactions with various alkyl and aryl isothiocyanates.[75] Acyl and alkoxycarbonyl isothiocyanates react with alcohols under neutral conditions, although yields are generally below 75% and hindered alcohols in particular give low yields. The isothiocyanates are generated in situ. An example is shown in Eq. 25.[77]



(Eq. 25)

O-Alkyl-*N*-cyclohexyl selenocarbamates are prepared by treating the alcohol with KH followed by cyclohexyl isoselenocyanate.[78]

Tertiary Alcohols. Special considerations that apply to the reduction of tertiary alcohol derivatives are discussed later and center on the tendency of tertiary xanthates and some related *O*-thioacyl derivatives to undergo facile, cyclic elimination to form alkenes (the Chugaev reaction). When this process is retarded or prevented by steric factors or by the presence of adjacent, electron-withdrawing groups in the alcohol, thioacylation can often be achieved using the methods described in the previous section, sometimes with minor modifications. Thus, *S*-methyl xanthate **31**[40] and imidazolide **32**[79] are prepared under standard conditions, and the *O*-(phenoxythiocarbonyl) derivative **33**[80] is obtained by deprotonating the alcohol with NaH, followed by the addition of PTC-Cl.



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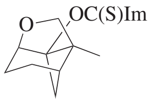

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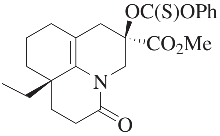
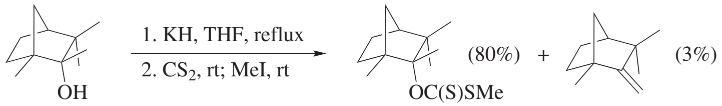


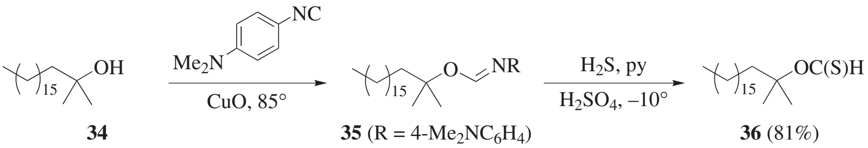
33

However, for tertiary alcohols in which the hydroxyl group is in a hindered, predominantly hydrocarbon-like environment, both alcohol deprotonation and xanthate stability can pose problems. For xanthates that are stable at ambient temperature, deprotonation of the alcohol with KH allows their synthesis with minimal olefin formation (Eq. 26).[81]



(Eq. 26)

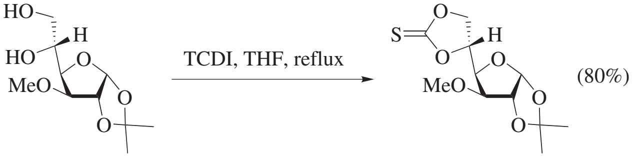
When the xanthate is too unstable, as is the case with alcohols such as **34**, an alternative is to deoxygenate the corresponding *O*-thioformate, which has much greater thermal stability. However, as noted in an earlier section, the iminium salt route cannot be used because the intermediate (*tert*-ROCH=NMe$^+_2$ Cl$^-$) rapidly decomposes to afford carbenium-ion-derived products. An ingenious alternative (Scheme 4) involves the CuO-catalyzed reaction of the alcohol with 4-(dimethylamino)isocyanobenzene to produce the formimidate **35**, which is thiolysed under near-neutral conditions to afford the desired *O*-thioformate **36**.[33]



Scheme 4

Diols. Examples of mono-thioacylation of diols and polyols in substrates where the formation of cyclic products is not an issue, either by virtue of intrinsic structure or by choice of reagent, have been provided in earlier sections (Eqs. 17 and 22).

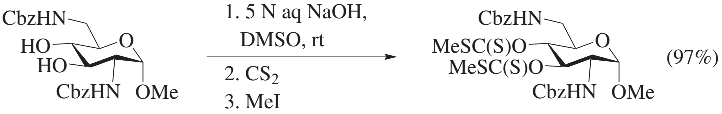
Cyclic *O,O*-(thiocarbonyl) derivatives of diols (cyclic thiocarbonates) are usually prepared by heating with TCDI in inert solvents. A simple example is shown in Eq. 27.[82] These reactions are promoted by 4-dimethylaminopyridine (DMAP).[83]



(Eq. 27)

The previously described, 2-pyridinone-derived reagent **28** will also carry out this transformation[74] and the more reactive combination of thiophosgene with DMAP is used to prepare a *trans*-fused thiocarbonate.[84]

For the conversion of 1,2-diols into *O*,*O*-bis(thiocarbonyl) derivatives prior to free-radical olefin formation, the standard conditions that were described earlier for mono-functionalization are generally applicable, as illustrated by the example in Eq. 28.[61] Reagents such as TCDI are not suitable for bis-functionalization of *trans*-diequatorial diols because of cyclic thiocarbonate formation.[85]



(Eq. 28)

S-(2-Cyanoethyl) xanthates are prepared from nucleosides using aqueous sodium hydroxide in DMSO, with 3-bromopropionitrile in the alkylation step.[86,87] This base-solvent combination is also used to prepare bis[*O*-(*N*-phenylthiocarbamoyl)] derivatives.[88]

The Reduction Step

Secondary Alcohol Derivatives

General Considerations when Selecting the *O*-Thioacyl Derivative and the Reducing Agent. For secondary alcohols, a variety of combinations of ROC(S)Y and reducing agents (MH) react efficiently to provide the deoxygenated product. As a consequence, the choice of Y may be made largely on the basis of the ease of thioacylation of the substrate structure, i.e. the level of steric hindrance around the targeted hydroxyl group and the sensitivity of the molecule to the various conditions for forming ROC(S)Y, which vary from neutral to strongly basic, as discussed in the foregoing section.

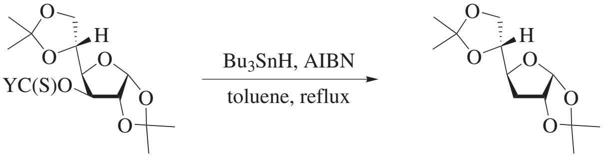
The advantages and disadvantages of the various reducing agents are discussed in the subsections that follow. The majority of the reported reductions use Bu_3SnH, and comparisons for this reagent are available for all variations in Y. For other MH species, comparisons within a set of standard substrates are usually available.

Limitations fall into two categories, and can apply to all substrate types; they may result from fragmentation, cyclization, or rearrangement of the intermediate radicals; or they may be a result of interactions of the MH species with other functional groups in the substrate. Limitations are discussed and exemplified largely in the context of reductions of secondary substrates with Bu_3SnH. When information is available, specific advantages or limitations to using other MH reagents are presented in the appropriate sections.

Reductions with Stoichiometric Amounts of Bu_3SnH. *Scope of Deoxygenations.* Despite the development of alternative, stannane-based systems and the other MH-based systems described later, approximately 80% of the deoxygenations recorded in the "Tabular Survey" use Bu_3SnH. The toxicity of organotin compounds and the issues associated with work-up and product purification, discussed in the "Experimental Conditions" section, have clearly not posed significant problems for laboratory-scale reductions, although they preclude industrial application. Reductions with Bu_3SnH benefit from the powerful hydrogen-donating ability of the reagent: k-values for abstraction from Bu_3SnH by alkyl radicals are in the $10^6-10^7\ s^{-1}$ range.[11] In terms of the general mechanism presented earlier, this means that essentially all of the post-fragmentation R• species will be converted into the desired deoxy compound (RH). Obtaining a high yield requires that appropriate reaction temperatures and concentrations are selected to optimize fragmentation over trapping of the initial, adduct radical. In general, it is beneficial to keep the substrate concentration low, either by operating in dilute solution or by inverse addition of the substrate plus initiator to a solution of Bu_3SnH.

No comprehensive studies of the effect of varying the Y group in reductions of ROC(S)Y with Bu_3SnH under precisely controlled conditions are available. However, results obtained for two commonly employed test substrates, *O*-thioacyl derivatives of 1,2:5,6-diisopropylidene-α-D-glucofuranose (Fig. 1)[39,68,72,89,90] and of cyclododecanol (Fig. 2),[39,77,91,92] which do involve some variations in the conditions and in the method used to determine the yield, demonstrate that good to excellent yields may be obtained with a variety of different Y groups and that initiation by azo compounds or by the Et_3B-O_2 system are equally effective for these substrates.

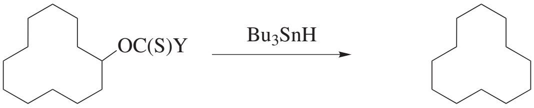
With respect to substrate scope some selected examples, taken with those shown in both earlier and later sections, serve to illustrate the tolerance of diverse structural features to deoxygenations using Bu_3SnH. Almost all of the commonly used blocking groups for O, N, and S are unaffected under typical deoxygenation conditions; in the "Tabular Survey," Tables 2A and 2B showing carbohydrate and nucleoside derivatives are replete with such examples, which also demonstrate that *O*-sulfonates and all types of C–F bonds are unchanged. Free hydroxy and amino groups are unaffected, but thiols and carboxylic acids are best protected.



Y	Yield (%)	Ref.
MeS	85	89
Im	74	66
PhO	79	90
C_6F_5O	100[a]	68
PhNH	96	39

[a]The yield was determined by ^{1}H-NMR analysis.

Figure 1. Effect of the thiocarbonyl substituent on yields in Bu_3SnH reductions of 3-O(CSY) derivatives of 1,2:5,6-di-*O*-isopropylidine-α-D-glucofuranose.



Y	Conditions	Yield (%)	Ref.
MeS	Et_3B, O_2, benzene, rt	93	91
PhO	Et_3B, O_2, benzene, rt	88	91
PhO	AIBN, toluene, 80–100°	68	92
PhNH	AIBN, benzene, reflux	88[a]	39
AcNH	AIBN, benzene, reflux	88[a]	77

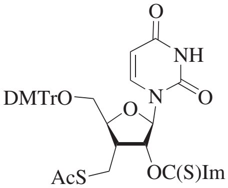
[a]The yield was determined by GC analysis.

Figure 2. Effect of the thiocarbonyl substituent and the initiator on yields in Bu_3SnH reductions of OC(S)Y) derivatives of cyclododecanol.

Strongly nucleophilic amino groups are usually protected to ensure selectivity for the hydroxy group in the thioacylation step. Most C−S bonds are stable under the usual reduction conditions. Although Bu_3SnH will generate alkyl radicals from phenylthioalkanes via an S_H2 mechanism,[11] scission of the C−SPh bond is not competitive with typical deoxygenations. Other C−SR bonds are also stable, even when electron-withdrawing groups are attached to the sulfur atom. Examples include the *S*-glycoside **37**,[93] the acetylthio compound **38**,[94] and the trifluoromethylthio nucleoside **39**.[95]

Sulfoxides, including those with a stereogenic sulfur center,[96] are unaffected, and sulfones are inert to Bu_3SnH, although reductive desulfonylation can occur by indirect mechanisms in the case of vinyl, allyl, and β-keto sulfones.[97] As discussed later, alkyl- and acyl- C−Se bonds are rapidly cleaved by Bu_3SnH under free-radical conditions.

37



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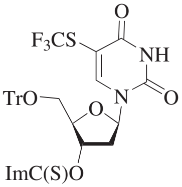
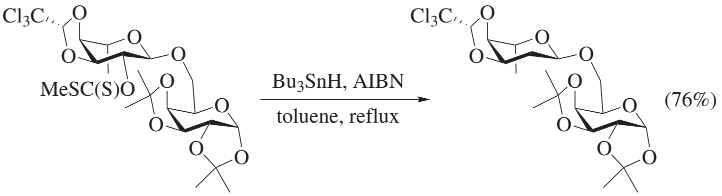


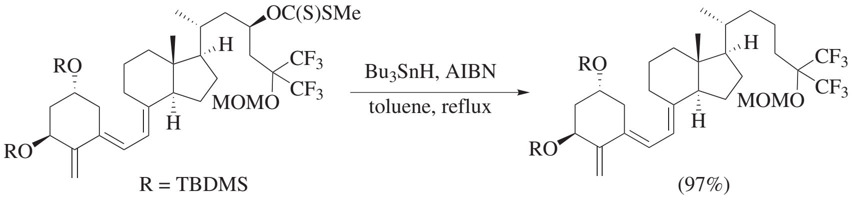
39

The rapid rate of reduction of *O*-thiocarbonyl derivatives can allow the preservation of groups that are reduced under more forcing conditions. An example where a trichloromethyl group survives is shown in Eq. 29,[98] although dechlorination of similar acetals by Bu$_3$SnH is also known.[99]

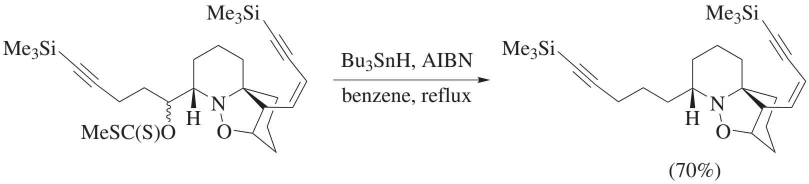


(Eq. 29)

Additions to alkenes, including terminal ones, and internal alkynes are not an issue. However, no example of a deoxygenation of a substrate bearing an unprotected, terminal alkyne is known, suggesting that addition of Bu$_3$SnH might be a competing process. Conjugated systems also survive, as shown by the triene in Eq. 30[100] and the *C*-(trimethylsilyl)enyne in a substrate that also contains a readily reducible N–O bond (Eq. 31).[101]



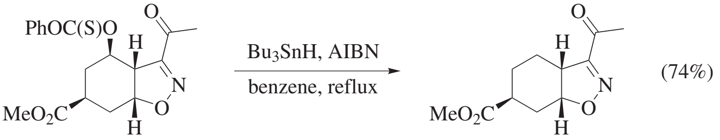
(Eq. 30)



(Eq. 31)

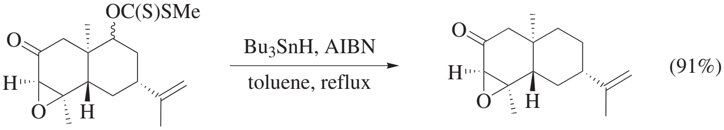
In the deoxygenation of a secondary, internal 1,3-diyne-5-ol, competing addition is seen in the presence of an excess of the reducing agent.[102]

Bu_3SnH in methanol will reduce ketones, especially the more electrophilic ones, by an ionic process,[11] but addition to the carbonyl group under aprotic, free-radical conditions is extremely slow. Consequently, ketones, including conjugated enones, do not need to be protected for stannane-mediated deoxygenations. Examples from the steroid arena include A-ring ketones[103] and enones,[104] 17-ketones,[77] and 17-acetyl derivatives.[105] Eq. 32 shows a substrate containing a cyclic, α-oximino ketone system.[106] Protection of aldehydes is advisable, although a deoxygenation in the presence of a hindered aldehyde is known.[107]



(Eq. 32)

Except when they are β to the intermediate carbon radical (see later), small rings, including epoxides, are also stable, even when adjacent to a ketone (Eq. 33).[108]

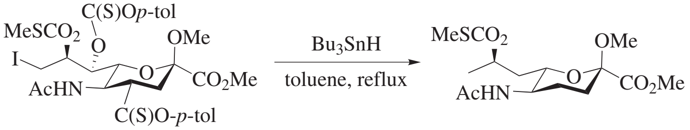


(Eq. 33)

Limitations. As noted earlier, problems encountered during free-radical reductions with Bu_3SnH and related systems involve either discrete interactions of the reducing agent with other functional groups in the molecule or fragmentations or cyclizations of the intermediate carbon-centered radicals. Competitive functional-group reductions often correlate with alkene-forming carbon-heteroatom β-fragmentations, and the addition of ring strain can bring otherwise unreactive bonds into play in both fragmentations and rearrangements.

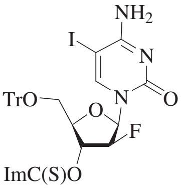
Reduction of C–Halogen Bonds. The well-established use of Bu_3SnH for reducing chloro-, bromo-, and iodo compounds[11] can pose selectivity problems in deoxygenations. However, C–F bonds are stable and competing reduction of C–Cl bonds is an issue only in activated cases such as benzylic chlorides and, as noted earlier, trichloromethyl groups under some conditions. Although direct measurements of the rates of reduction of *O*-thioacyl compounds by Bu_3SnH are not available, they are expected to be in the 10^7–10^8 s^{-1} range, based on the similar rate found for reductions with $(TMS)_3SiH$.[109] Consequently, all sp^3 C–Br bonds pose potential problems, since k-values for their reactions with $Bu_3Sn\bullet$ are in the same range.[11] If a deoxygenation needs to be conducted in the presence of this functionality, the systems based on B–H[110] and O–H[38,111] donors described later are safer choices, since both Si–H[109] and P–H[112] based reagents reduce bromoalkanes. Because of the higher energy of sp^2 carbon-centered radicals, bromoalkenes and bromoarenes (and the corresponding chloro compounds) normally survive deoxygenation reactions. An example is found in the "Applications to Synthesis" section (Eq. 94). Bromoarenes are reduced by Bu_3SnH under UV irradiation.[11]

All iodoalkanes are reduced competitively. For the MeI + $Bu_3Sn\bullet$ reaction, $k = 2.5 \times 10^9\ s^{-1}$.[11] An example of reduction of both iodo and *O*-(aryloxythiocarbonyl) functions in a carbohydrate derivative is shown in Eq. 34.[113]



(82%) (Eq. 34)

The examples of nucleosides **40**[114] and **41**,[87] in which the iodine is attached to an sp^2-hybridized carbon, give different results in reductions with Bu_3SnH, such that reduction of the C–I bond is observed in the former case and retention is observed in the latter.



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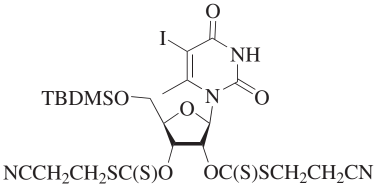
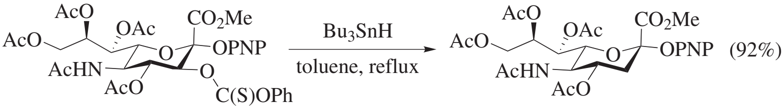


41

The $Bu_3B{-}H_2O{-}O_2$ system does not reduce iodoarenes[111] and would be the safest choice to ensure selective deoxygenation over de-iodination when this group is present.

Reduction of C–N Bonds and Nitrogenous Substituents. Although most C–N bonds, including those in imines and nitriles, are unaffected by Bu_3SnH, isocyanoalkanes are reduced to alkanes at a rate competitive with *S*-methyl xanthate reduction.[115] Isocyanoarenes also react, adding Bu_3SnH without C–N scission. The reduction of the C–N bond in aliphatic, allylic, and benzylic nitro compounds by Bu_3SnH is also well established.[116–118] Tertiary and activated nitro compounds are reduced under relatively mild conditions, but the requirement of higher reagent concentrations and reaction temperatures for secondary nitro compounds suggests that they could be retained in typical deoxygenations in dilute solution. Non-activated, primary nitro compounds are not reduced by Bu_3SnH. Silanes also react with aliphatic nitro compounds under free-radical conditions, reducing the O–N bonds.[109] The stability of nitro groups under deoxygenation conditions using B–H, C–H, O–H, and P–H donor systems has not been examined.

For aromatic nitro compounds and Bu_3SnH, the situation is not so clear. An *O*-(4-nitrophenyl) glycoside survives (Eq. 35),[119] but attempted deoxygenation of an *O*-(4-nitrothiobenzoate) fails.[1] 1,3-Dinitrobenzene inhibits free-radical processes, so it is likely that other nitro arenes bearing electron-withdrawing substituents will pose problems.



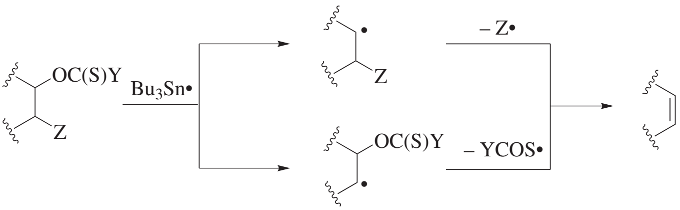
(Eq. 35)

An ambivalent situation also obtains with substrates containing azido groups. Retention of the group is seen in some cases,[120–122] but reduction to the amine can also take place.[123] Complex mixtures are reported in one example[124] and a combination of retention and β-elimination in another.[125]

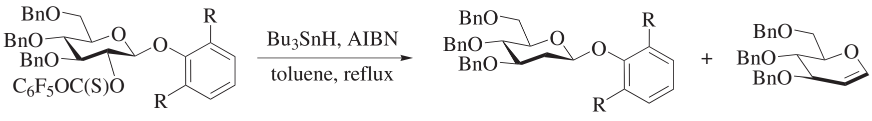
Reduction of C–Se Bonds. As noted earlier, alkylselenium and acylselenium bonds are rapidly reduced by Bu_3SnH, a process that forms the basis of deoxygenations of phenylselenoformates of alcohols[126] discussed in the “Comparison with Other Methods” section.

Fragmentations. Useful, radical-based methods for alkene formation from various types of β-substituted alcohols involve the processes shown in Scheme 5, but from the viewpoint of simple deoxygenations, these eliminations impose structural limitations.

Apart from –OC(S)Y species (see later discussion, and Table 5), groups of the type Z = OR (Scheme 5) are rarely expelled, although a special case is found for Z = *O*-aryl, when steric compression is also present (Eq. 36).[127]



Scheme 5

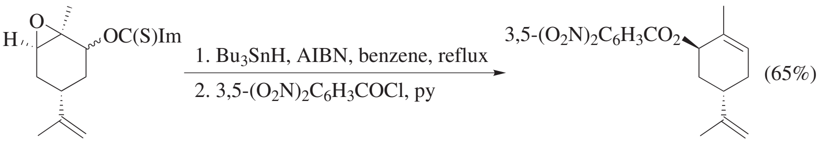


R	Yield (%)	
H	100	—
OMe	10	major

(Eq. 36)

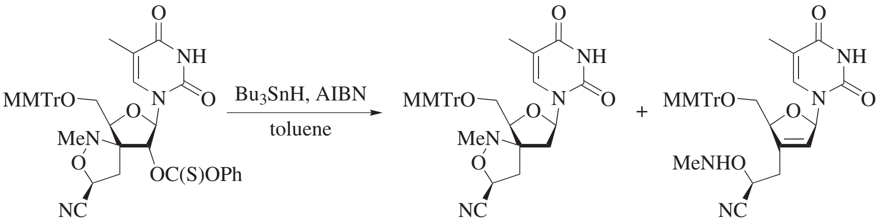
Alkene formation from other heteroatomic species according to Scheme 5 is facile when Z = NC,[115,128] NO_2,[117,129] SPh,[130] and SO_2R.[131] As noted earlier, an elimination when Z = N_3 is known.[125] When a potentially fissile C–S bond is contained in a tetrahydrothiophene ring, generating a radical at C3 does not lead to C–S scission.[132,133]

Ring-Opening Processes: C–O and C–N Bonds. Ring strain or, less frequently, special structural features can lead to β-scission of *C*-heteroatom bonds that would not otherwise cleave. Oxirane rings usually open to generate alkoxy radicals, which either give the allylic alcohol by *H*-abstraction (Eq. 37) or participate in further, intramolecular processes, depending upon the substrate and the conditions.[134] Ring opening of β-oxiranyl radicals by the alternative C–C fragmentation is seen when the derived radical is suitably stabilized.[135]



(Eq. 37)

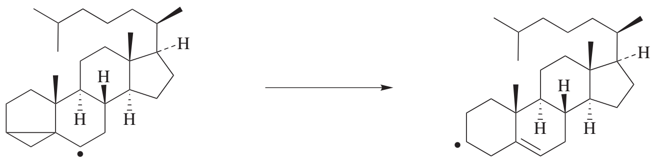
Aziridines behave in a similar way,[136] and C–N cleavage in a spiro isoxazolidine system is also known (Eq. 38).[137] In the context of the latter reaction, and deoxygenation reactions at the ribose 2-position in nucleosides in general, cleavage of the sugar-base C–N bond is not observed.



MMTr = monomethoxytrityl

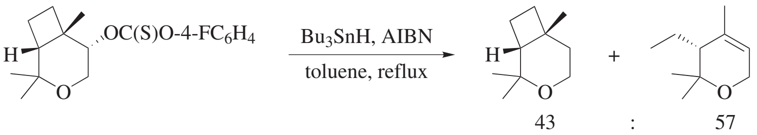
(Eq. 38)

Ring Openings and Other Rearrangements: C–C Bonds. The ring opening of cyclopropylcarbinyl radicals is one of the most rapid processes in free-radical chemistry. For both the rearrangement shown in Eq. 39 and the same reaction of the parent cyclopropylcarbinyl radical, rate constants are in the 10^7–10^8 s^{-1} range at ambient temperatures.[138]

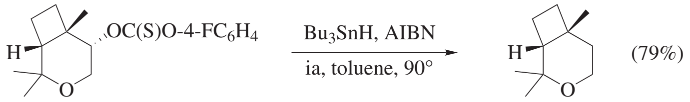


(Eq. 39)

Although these reactions are reversible, only special substitution patterns will preserve the cyclopropane ring or form it from the acyclic radical precursor.[139] Cyclobutylcarbinyl radicals fragment slower than their cyclopropyl counterparts,[140] and the process may be subject to control by suitable choice of conditions. In a tricyclic system, only ring opening is seen[84] but in a bicyclic system (Eq. 40a)[141,142] refluxing the premixed reactants in toluene gives a 43:57 ratio of simple reduction to fragmentation; a high yield of the desired reduction product is obtained by inverse addition of the substrate at 90° (Eq. 40b).

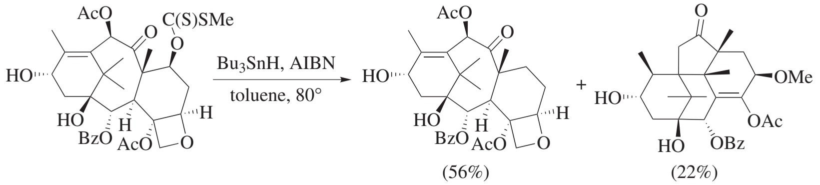


(Eq. 40a)



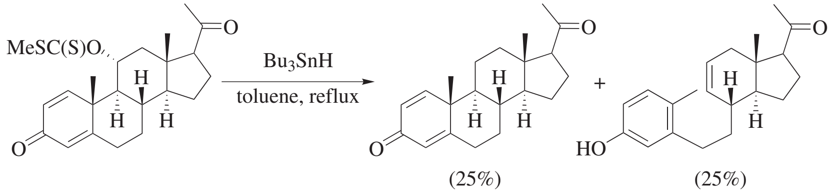
(Eq. 40b)

Other rearrangements triggered by carbon-centered radicals frequently involve combinations of steric compression, ring strain, and stabilization of the newly formed radical. Rearrangements in the taxane system may be complex, as illustrated in Eq. 41, where the carbon atom in the methyl ether in the rearranged material is derived from the carbon skeleton, not the thiocarbonyl group.[143] With Ph_3SnH the same product ratio is seen, in addition to some direct reduction of the xanthate group to the corresponding methyl ether, but with the weaker H-donor tris(trimethylsilyl)silane [$(TMS)_3SiH$] only rearrangement products are observed.



(Eq. 41)

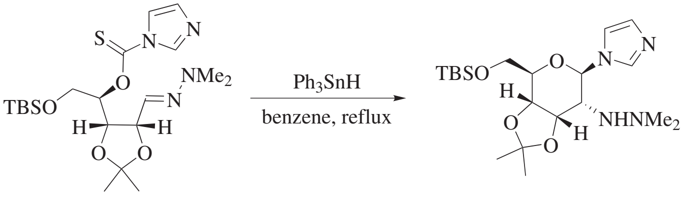
In a deoxygenation at C11 in a steroid A-ring dienone, competitive fragmentation of the C9−C10 bond is driven by the formation of a stabilized aryloxy radical (Eq. 42).[60]



(Eq. 42)

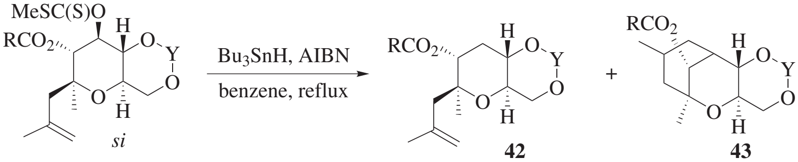
Neophyl-type rearrangements in 7-azabenzonorbornenol derivatives also take place under deoxygenation conditions.[144] Ring expansions and annulations utilizing a variety of radical-generating methods have been reviewed.[145]

Cyclization Processes. Ring formation by the addition of carbon-centered radicals to multiple bonds is a valuable synthetic tool,[139] but synthetic designs that incorporate a simple deoxygenation must clearly avoid the structural features that would lead to such cyclizations, from both the primary adduct radical and the deoxy radical formed by the subsequent C−O scission. Trapping the adduct radical with an alkene was discussed earlier (Eq. 5), and an example involving a C=N system, in which the $-SSnPh_3$ group is removed by a second reductive step, is shown in Eq. 43.[23] In this case, replacing triphenylstannane (Ph_3SnH) with Bu_3SnH affords the simple deoxygenation product, a result that is counterintuitive with respect to the somewhat better *H*-donating ability of Ph_3SnH but consistent with increased steric interactions in the initial adduct radical, facilitating the C−O cleavage.



(56%) (Eq. 43)

In general, the molecular architecture that permits a 5-exo-trig cyclization presents the greatest potential for competition. An example is shown in Eq. 44 in which the simple reduction product **42** predominates over the cyclization product **43** when higher concentrations of the substrate are used.[58]



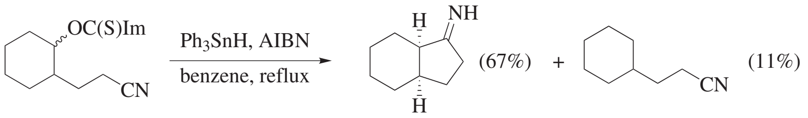
si **42** **43** (Eq. 44)

Y = Si(t-Bu)$_2$
R = PMBO(CH$_2$)$_3$

	Yield (%)	
[M]	**42** + **43**	**42**:**43**
0.125	90	>95:5
0.003	50	<5:95

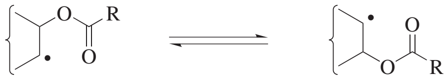
[M] = initial substrate molarity

Cyclizations onto alkenes to form 6-membered rings are less common, since abstraction of any available, allylic hydrogen is usually favored. A related, intramolecular abstraction from a cyclic acetal has been reported in a deoxygenation reaction.[146] Cyclization onto a nitrile is also known, and can be the dominant process when an electron-rich, intermediate radical is involved (Eq. 45).[147]



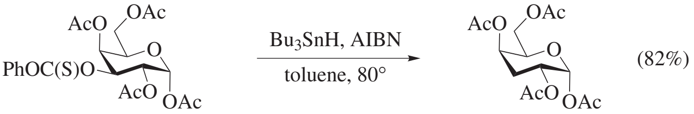
(Eq. 45)

Acyloxy Migrations and Related Processes. Isomerization of β-acyloxy radicals (Eq. 46) is facile when sufficiently exothermic, and similar rearrangements and fragmentations of β-phosphatoxy radicals are intimately involved in radical-induced damage to nucleic acids. These processes have been comprehensively reviewed.[148]



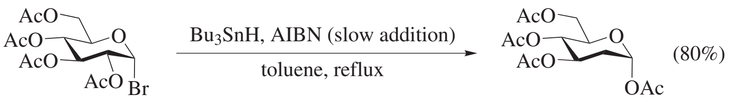
(Eq. 46)

The migration is a concerted, suprafacial, reversible process. Analogous rearrangements of γ-acyloxy radicals do not take place. The process is driven by direct or indirect radical stabilization and when stabilization of one radical relative to the other is not significant, rearranged products are not observed. An example is shown in Eq. 47, where no constitutionally isomeric deoxygenated products derived from migration of either of the two available β-acetoxy groups are observed.[149]



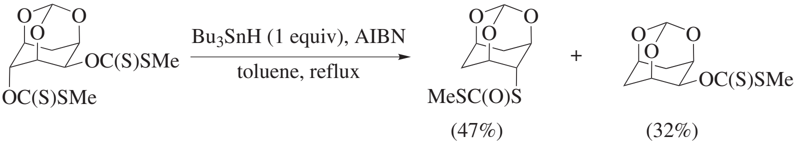
(Eq. 47)

Although recorded reductions of *O*-thioacyl derivatives provide no unambiguous examples, reactions using chloro- or bromo compounds as precursors[148] serve to illustrate potential problems. Acyl migration occurs between secondary centers, from C2 to C1 in carbohydrate derivatives. This process is driven by anomeric stabilization of the newly formed C1–O bond in the rearranged radical, and provides a route to 2-deoxysugars from 1-bromo-1-deoxysugars.[150] Eq. 48 shows a typical example.[150]



(Eq. 48)

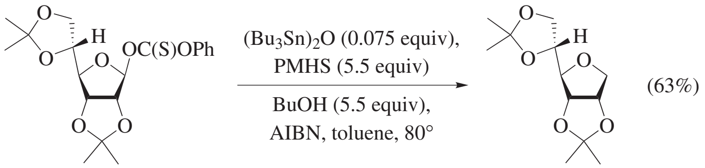
An apparent antarafacial acyloxy migration, observed during the deoxygenation of a taxol-related *S*-methyl xanthate[143] and requiring the conversion of a tertiary to a secondary radical, is ascribed to an anionic benzoate migration in the thioacylation step by analogy with a closely related system.[151] Most *O*-thiocarbonyl groups do not undergo 1,2-thioacyl migrations because β-elimination to form the alkene is preferred, as described later. A 1,3-transfer of a xanthate is known (Eq. 49).[30]



(Eq. 49)

1,4- and 1,5-Migrations of aryl groups, attached to silicon in disilanes or to the sulfonyl group in *O*-(arenesulfonates), to secondary radical centers are also known, although very low concentrations of Bu_3SnH must be maintained.[152]

Reductions with Catalytic Systems and with Other Stannanes. *Catalytic and Polymer-Bound Systems.* Reaction conditions that successfully employ sub-stoichiometric amounts of a tin reagent require specific reagent/substrate combinations for the in situ Sn−H regeneration step. Whereas borohydrides ($NaBH_4$, $NaBH_3CN$) allow reductions of organic halides that are catalytic in the tin reagent, similar deoxygenations require a silane as the stoichiometric reducing agent and are limited to *O*-(aryloxy- or alkoxythiocarbonyl) derivatives. *O*-(Phenoxythiocarbonyl) derivatives are reduced in a homogeneous system with a catalytic amount of $(Bu_3Sn)_2O$ and an excess of both poly(methylhydrosiloxane) [$HO(MeSi(H)O)_nH$, $n \sim 35$; PMHS] and 1-butanol; the latter additive assists both the initial generation of Bu_3SnH and its regeneration from Bu_3SnOAr. The reported yields are similar to those obtained using Bu_3SnH in stoichiometric amounts (Eq. 50).[92] This reagent combination also reduces *O*-(pentafluorophenoxythiocarbonyl) derivatives,[153] and a similar system without added butanol reduces *O*-(methoxythiocarbonyl) nucleosides.[71]

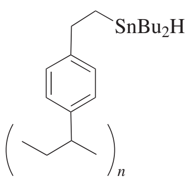


(Eq. 50)

$NaBH_3CN$ in *tert*-butanol will reduce Bu_3SnSMe, the co-product from *S*-methyl xanthate-Bu_3SnH reactions,[105] but apparently this has not been used as an in situ regeneration method with sub-stoichiometric amounts of the stannane.

Two polystyrene-bound stannanes **44** and **45** have been described for deoxygenations. They offer the advantage of maintaining all of the tin compounds in an insoluble form, thereby facilitating work-up and minimizing the issue of product contamination.

Reductions of both ROC(S)OPh and ROC(S)SMe species using **44** (approximately two equivalents)[104,154] are carried out under standard conditions. Active reagent is regenerated in a separate step by treatment with iodine followed by diisobutylaluminum hydride.[154] Reaction times are longer than for Bu_3SnH, but yields are comparable for standard substrates[104] and range from modest to high for



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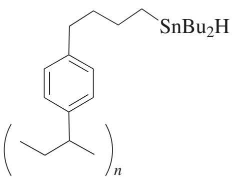
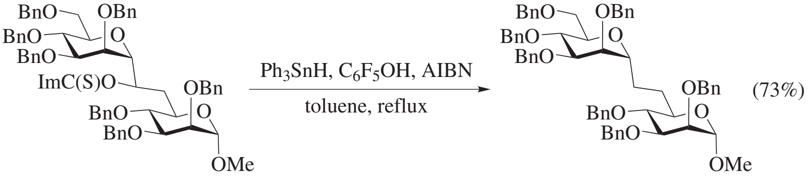


45

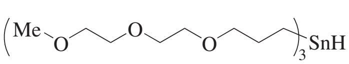
reductions of a series of 1,3-dioxane derivatives.[155] Polymer **45** is used in catalytic amounts with in situ regeneration using excess trimethoxysilane and 1-butanol. Three standard ROC(S)OPh substrates give yields similar to those obtained with Bu_3SnH.[156] Polymer-supported organotin reagents have been reviewed.[157]

Other Stannanes. Limited examples indicate that Ph_3SnH can replace Bu_3SnH. Improved yields have occasionally been reported[158] and an advantage in ease of purification noted in one instance,[159] but reduction of the thiocarbonyl group to methylene has also been observed in cyclic thiocarbonates[143] and *O*-thiobenzoates[15] and can be the major process under some conditions.[160] Room temperature reductions with this reagent using the $Et_3B{-}O_2$ initiation system give poor results relative to Bu_3SnH.[91] Ph_3SnH is the recommended reagent when combined with pentafluorophenol for reducing ROC(S)Im derivatives of carbon-linked disaccharides (Eq. 51).[161]



(Eq. 51)

Five modified stannanes (**46**–**50**) have been described, each bearing features that can facilitate product isolation. A base-soluble Sn(IV) catalyst for reducing halo compounds with $NaBH_4$ is available,[162] but this system is not suitable for deoxygenations. The polyether-containing reagent **46**[163] has appreciable water solubility; it is used to reduce alkyl halides, and should be applicable to deoxygenations.



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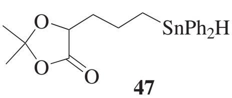

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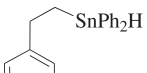

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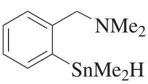

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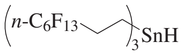
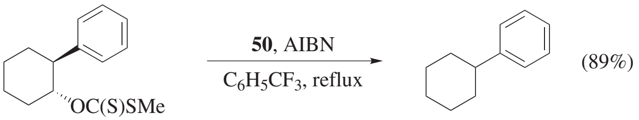


50

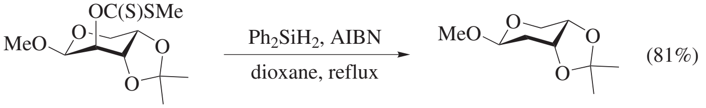
The dioxolanone derivative **47** deoxygenates a standard substrate efficiently and is removed from reaction mixtures by acidic or basic hydrolysis.[164] Acid does not fully extract the pyridine-derived reagent **48** and co-products, but the polarity of these materials facilitates chromatographic product isolation in deoxygenations of non-polar substrates.[165] The alternative, more basic reagent **49** is different in character. As a result of internal activation by nitrogen-tin coordination it is more "hydride-like" than Bu_3SnH, and will readily reduce ketones. In non-polar solvents, **49** will carry out normal, free-radical reductive chemistry, including a deoxygenation, but the reduced thermal stability relative to other stannanes requires that excess reagent be employed.[166] "Fluorous" technology, which exploits the mutual, low solubility of polyfluorinated organic compounds and their hydrogen counterparts, has also been applied to stannane-mediated reductions. Compound **50** deoxygenates *S*-methyl xanthates in benzotrifluoride (Eq. 52). A partitioning work-up separates the product from excess reagent and reagent-derived co-products.[167]



(Eq. 52)

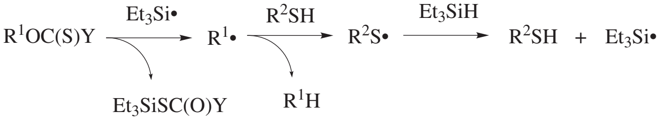
Reductions with Reagents Containing Si–H, Ge–H, and Ga–H Bonds. Reagents based on Si–H donor systems and other non-tin MH systems for applications to free-radical chemistry have been reviewed.[13,168] Most of these reagents have been used in deoxygenations and are discussed in this and the following sections.

Silanes offer reduced toxicity relative to stannanes, and the volatility of simple silanes can also be advantageous when a large excess of the reagent is used. Although silyl radicals add rapidly to thiocarbonyl groups, a key step in the propagation sequence—the reaction of the carbon-centered radical with the *H*-donor—is slower for simple silanes such as Et_3SiH than for their tin counterparts, by a factor of approximately 700.[169,170] This rate difference, in combination with non-productive reactions of silyl radicals with aromatic hydrocarbons[170] and with peroxide initiators,[171] results in short chain lengths. Modifications to the reaction conditions typically employed for Bu_3SnH-mediated reactions are necessary to carry out efficient reductions with most monosilanes. For Et_3SiH and similar trialkylsilanes, two methods are available. *S*-Methyl xanthates and related ROC(S)Y species are reduced in neat Et_3SiH at reflux (108°) by the gradual addition of up to one equivalent of benzoyl peroxide (Bz_2O_2).[171] Reactions using phenylsilane ($PhSiH_3$) are conducted in toluene or xylene with two equivalents of the silane and the gradual addition of Bz_2O_2 or AIBN.[172] For reductions using diphenylsilane (Ph_2SiH_2) initiation by $Et_3B–O_2$ (air) is recommended,[173] although AIBN is also effective.[174] Under the $Et_3B–O_2$ conditions, $PhSiH_3$ is ineffective and triphenylsilane (Ph_3SiH) is somewhat inferior to Ph_2SiH_2.[173] On a per-mole cost $PhSiH_3$, which is an air-stable, volatile liquid, is the least expensive reagent.[172] Yields with these systems are generally high. A reduction using Ph_2SiH_2 is shown in Eq. 53.[174] *O*-Thiocarbamates are reduced with neat Et_3SiH plus Bz_2O_2 in a sealed tube at 140°.[75]



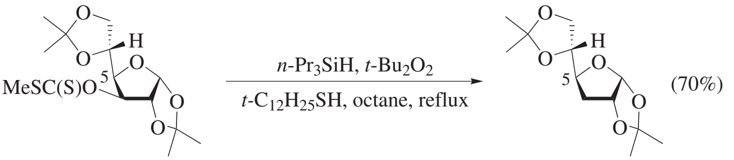
(Eq. 53)

An alternative strategy[170,175] utilizes the concept of polarity reversal. Although alkyl radicals abstract a hydrogen atom relatively slowly from simple silanes, they do so rapidly from a thiol (k_{rel} for *t*-BuSH vs. Et_3SiH is approximately 1400). The thiyl radical that is generated does not add to thiocarbonyl groups, but will readily abstract a hydrogen atom from R_3SiH, thereby acting as a chain carrier (Scheme 6).



Scheme 6

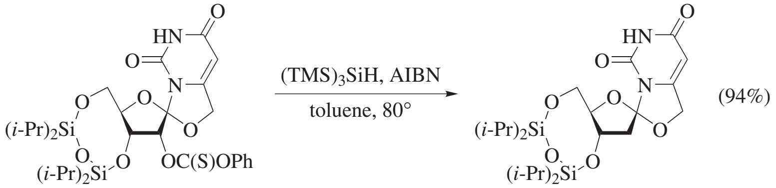
Reactions are conducted in non-aromatic, hydrocarbon solvents with 0.02–0.04 equivalents of the initiator (a non-polar peroxide is preferred) and the thiol. Various thiols, of which the most frequently used is *tert*-dodecanethiol (t-$C_{12}H_{25}SH$, a mixture of isomers), can be employed. A typical reduction is shown in Eq. 54.[170] Reductions of *S*-methyl xanthates with Ph_3SiH do not require the separate addition of a thiol since this silane reduces COS to generate triphenylsilanethiol (Ph_3SiSH), which is effective in the polarity reversal process.[176]



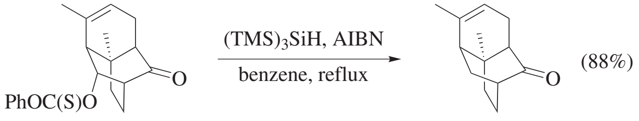
(Eq. 54)

In the reaction shown in Eq. 54 a small amount of epimerization at C5 is seen, which is ascribed to the ability of either the silicon-centered radical or the thiyl radical to abstract the tertiary hydrogen atom from that position. Deliberate epimerizations at such tertiary centers have been achieved with initiator-thiol combinations in the absence of MH species.[177]

By lowering the Si–H bond energy, reagents are obtained that are more "Bu_3SnH-like." Although substituting aryl for alkyl in silanes only slightly improves the *H*-donor ability,[169] incorporating Si–Si bonds affords a more marked effect. The most widely used silane of this type is $(TMS)_3SiH$. The diverse reducing abilities of this compound have been extensively studied by Chatgilialoglu,[109,178] and both his group[109] and others[90,173] have explored reactions with *O*-thioacyl compounds. The derived silyl radical adds rapidly and reversibly to thiocarbonyl groups and the subsequent rate of hydrogen donation to the fragmentation-derived radical is approximately one hundred times greater than with Et_3SiH.[109] This property allows reactions to be run with catalytic quantities of the initiator (usually AIBN or the $Et_3B{-}O_2$ combination) and does not require the slow addition of reactants. $(TMS)_3SiH$ has been used to deoxygenate a variety of secondary substrates; examples include an unusual nucleoside (Eq. 55)[179] and a patchoulol analog (Eq. 56).[180]



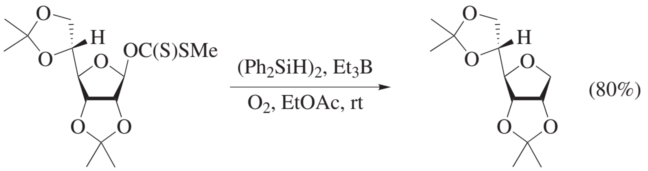
(Eq. 55)



(Eq. 56)

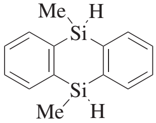
In the latter example, selective reduction in the presence of a ketone is attained despite the increased reactivity of $(TMS)_3SiH$, relative to Bu_3SnH, toward ketone carbonyl groups.[109] Aromatic ketones are considerably more reactive toward this silane and if this functionality is present, either Bu_3SnH or one of the reagents discussed in later sections is the safer choice. Relative rates of reductions by $(TMS)_3SiH$[109] indicate that no selectivity would be expected between an *O*-thioacyl substrate and an aliphatic iodo compound, and that only a ten-fold rate difference is available for the selective deoxygenation of a substrate containing a tertiary bromide. Efficient reductions with $(TMS)_3SiH$ using a micro-reactor flow system, with a five-minute residence time in toluene at 130°, have been reported for a variety of substrates. A primary C–Cl bond survives these conditions.[181] $(TMS)_3SiH$ adds to a terminal alkene during the course of a cyclic thiocarbonate deoxygenation,[182] and (*E*)-(*Z*) olefin interconversions have also been reported.[183] The related trisilane $(TMS)_2Si(H)Me$ appears to be equivalent to $(TMS)_3SiH$ for reductions, although examples are limited.[184] Tris(alkylthio) silanes such as $(i\text{-}PrS)_3SiH$ are also effective[185] and are easily made, but the liberation of large amounts of thiol upon work-up is clearly a disadvantage.

The aryl-substituted disilanes $(Ph_2SiH)_2$, $[(4\text{-}FC_6H_4)_2SiH]_2$, and $[PhSi(Me)H]_2$ will deoxygenate ROC(S)SMe and ROC(S)Im species. Of these disilane reagents, the first is the easiest to prepare and is an air-stable solid. Reductions are carried out in ethyl acetate with initiation either by AIBN or by the $Et_3B{-}O_2$ system (Eq. 57).[186]



(Eq. 57)

Several 9,10-dihydro-9,10-disilaanthracene derivatives have been investigated. Compounds **51** and **52** cleanly deoxygenate ROC(S)NHPh and ROC(S)OAr derivatives, but *S*-methyl xanthates give poor results.[76] The trimethyl compound **53** is less efficient. The monosilaanthracene **54** is ineffective, suggesting that a transannular Si-Si interaction may enhance the reactivity of the other reagents.



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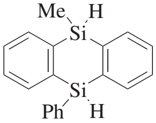

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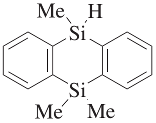

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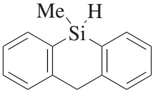

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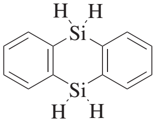
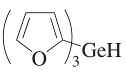


55

The parent 9,10-dihydro-9,10-disilaanthracene (**55**) also effects reductions of ROC(S)OAr substrates, but reactions with the other commonly used *O*-thioacyl derivatives fail to complete, even with excess reagent and initiator, suggesting that the accumulation of side products causes decomposition of the reagent.[187]

Reductants with Ge–H bonds have found applications in free-radical chemistry, primarily for the generation, from C–Br and C–I bonds, of radicals for inter- and intramolecular C–C bond-forming reactions. The Ge–H bond strength (Et_3GeH = 83 kcal/mol) results in longer radical half-lives relative to Bu_3SnH under the same conditions, and thereby promotes addition and cyclization processes over direct *H*-capture. Reductions of ROC(S)Y substrates with these reagents suggest that they are viable substitutes for Bu_3SnH, but they all suffer from the disadvantages of the relatively high cost of germanium compounds and the need to synthesize the reagent. Tris(2-furyl)germane (**56**),[188] tri-*n*-butylgermane (Bu_3GeH),[189] the mixed germanes **57** and **58**,[190] and two polymer-bound versions **59** and **60**[190] have all been used to reduce standard substrates. Satisfactory yields are obtained in all cases. In reductions using the polymer-bound species, a substantial excess of reagent is required to ensure complete reaction.



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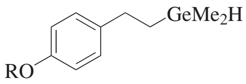
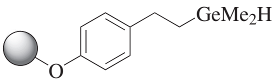


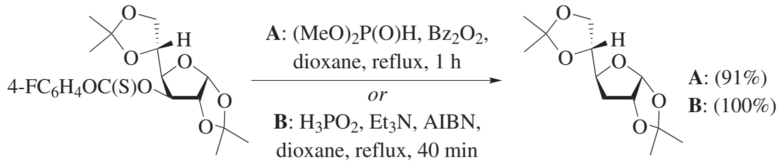
	R
57	Bn
58	H



	Resin
59	Merrifield
60	Quadragel

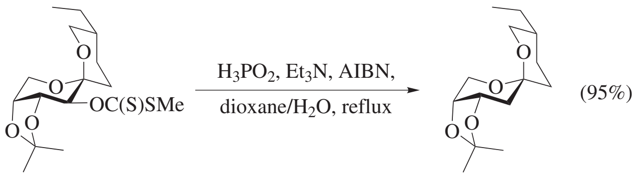
Dichlorogallane ($HGaCl_2$), a reagent of unknown structure generated in solution by reducing gallium(III) chloride in THF with either sodium bis(2-methoxyethoxy)aluminum hydride or diisobutylaluminum hydride, will carry out Et_3B-initiated reductions including one example of the deoxygenation of a secondary *S*-methyl xanthate. The reagent reduces alkyl bromides and iodides, but not ketones.[191,192] The analogous indium(III) species is known, but no reactions with ROC(S)Y species are described.[192]

Reductions with Reagents Containing P–H Bonds. Both dialkyl phosphites [$(RO)_2P(O)H$] and hypophosphorous acid (H_3PO_2) or its tertiary amine salts are effective and inexpensive reagents for deoxygenating *O*-thioacyl derivatives under conditions similar to those employed with simple silanes.[112,193,194] A competition experiment indicates that $(MeO)_2P(O)H$ is a slightly less efficient *H*-donor than Ph_2SiH_2.[194] Reductions using $(MeO)_2P(O)H$ or $(EtO)_2P(O)H$ are carried out in dioxane at reflux with excess reagent and with the gradual addition of Bz_2O_2. In H_3PO_2 reductions, inclusion of a tertiary amine (1.1–2 equivalents relative to H_3PO_2) is necessary to maintain neutral or mildly basic conditions when the substrate is acid sensitive.[193,194] The H_3PO_2 may be added as the commercial 50% solution, as the anhydrous acid, or as the crystalline salt (EPHP) formed with *N*-ethylpiperidine. For these reactions, AIBN is a satisfactory initiator. The reduction of a standard substrate with these P–H reagents is shown in Eq. 58.[193,194] The related reagents $(TMSO)_2P(O)H$ and $(t\text{-}BuO)_2P(O)H$ give poor yields, and phosphorous acid (H_3PO_3) is ineffective.



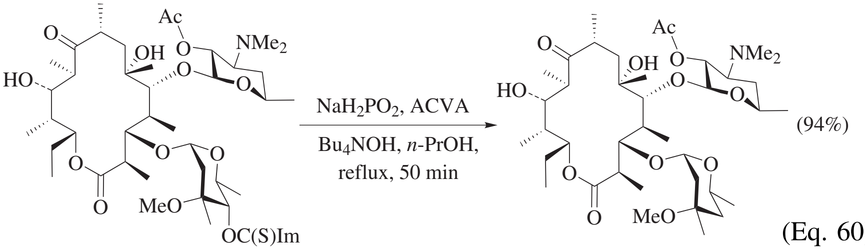
(Eq. 58)

The H_3PO_2-amine method can be applied to other substrates including nucleosides,[195] taxanes,[196] macrolides,[197] and diverse carbohydrate derivatives (see Table 2A of the "Tabular Survey"). A step in the synthesis of the talaromycins from D-fructose is shown in Eq. 59.[198]



(Eq. 59)

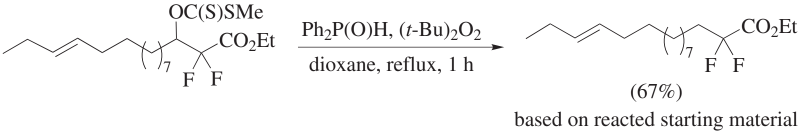
Modifications have afforded conditions for running reactions in hydroxylic solvents, including water. EPHP in combination with the water-soluble initiator 4,4′-azobis(4-cyanopentanoic) acid (ACVA) and a quaternary phase-transfer agent deoxygenates secondary xanthates in water. Large, lipophilic substrates tend to give incomplete conversions,[199] although this is not an issue using Et_3B-O_2 initiation.[200] Preformed tetraalkylammonium hypophosphites have also been used.[201] A single example indicates that sodium hypophosphite can be used in ethanol with AIBN initiation,[202] and a study for a multikilogram reduction of an erythromycin derivative also uses this salt in combination with phase-transfer agents in alcohol solvents (Eq. 60).[203] In this case the phase-transfer agent is generated by neutralizing the acidic initiator (ACVA) with tetrabutylammonium hydroxide. Effective reductions are also attained with H_3PO_2 in water, when the quaternary salt is bonded to a high-porosity polymer.[204]



(Eq. 60)

These simple P–H based reagents clearly offer a viable alternative to stannanes, with diminished issues with respect to toxicity and work-up. A problem with these reagents is their ability to add to alkenes, particularly when the neutral dialkyl phosphites are used. Dimethyl phosphite will readily add to the trisubstituted double bond in cholesteryl acetate under free-radical conditions.[194] Other functional groups, notably carbon-halogen bonds, are reduced by these reagents but comparative studies are not available to determine whether this might be an issue when reducing an *O*-thioacyl compound containing such functionality. In reductions using salts of H_3PO_2, the nucleophilic character of the anion should also be considered if substrates contain good leaving groups or Michael acceptors.

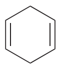
Di-*n*-butylphosphine oxide[205] and diphenylphosphine oxide[206] are also suitable *H*-donors. Sub-stoichiometric amounts of initiator, added in portions, are used. Only *S*-methyl xanthates have been reduced, but presumably all of the standard derivatives would react. Addition to carbon-carbon multiple bonds has been noted with these reagents, but interrupting reactions before completion affords acceptable yields (Eq. 61).[207]



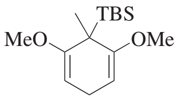
(Eq. 61)

Reductions with Reagents Containing C–H Bonds. Several systems that employ *H*-donors containing relatively weak C–H bonds are available; two are based on designed reagents that must be synthesized.

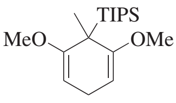
1,4-Cyclohexadienes are well-established *H*-donors, but the parent compound **61** is not suitable for deoxygenations because the highly stabilized radical will either not add to the thiocarbonyl group or, if it does add, simple reversal of the addition process will be preferred over the desired fragmentation of the R–O bond. However, several 3-methyl-3-(trialkylsilyl)-1,4-cyclohexadienes prove to be efficient reducing agents under free-radical conditions. Cyclohexadienes **62–64**, which are readily prepared by Birch reduction-alkylation procedures, have all been employed for deoxygenating ROC(S)Y species.[208,209]



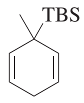
61



62

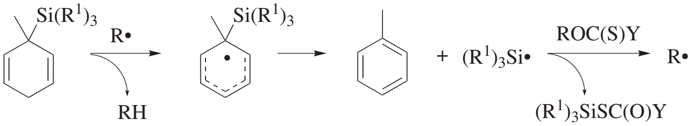


63



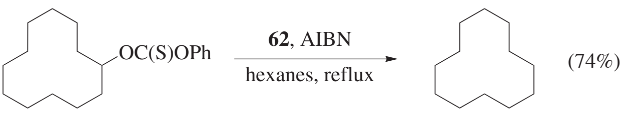
64

These reactions involve hydrogen atom abstraction from the methylene group followed by aromatization-driven expulsion of the trialkylsilyl radical (detected by ESR studies), which propagates the chain process (Scheme 7).



Scheme 7

Reduction yields for *S*-methyl xanthates and *O*-(phenoxythiocarbonyl) derivatives range from 68–91% and show no obvious dependence upon which diene is used over a range of examples, one of which is shown in Eq. 62.[209]

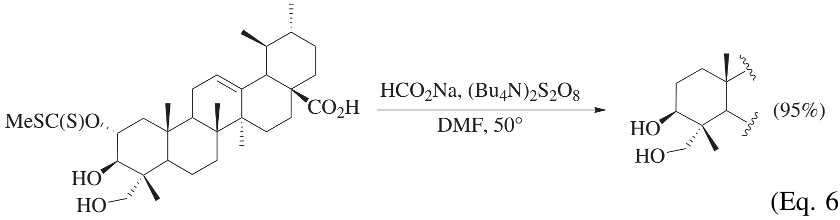


(Eq. 62)

Tris(trimethylsilyl)methane $(TMS)_3CH$, which reacts with alkyl radicals approximately four times slower than its silicon counterpart discussed earlier, is also an effective reagent. A 72% yield of 5α-cholestane is obtained from the corresponding 3β-xanthate[210] (structures **19** and **15**, respectively, in the "Mechanism and Stereochemistry" section). This reagent should be suitable for general application.

A versatile system using simple reagents is described by Kim and coworkers.[211] Formate ion (as HCO_2Na) is the *H*-donor, and tetrabutylammonium persulfate $[(Bu_4N)_2S_2O_8]$ provides sulfate radical anions for chain initiation by abstracting from HCO_2^-, thereby producing $CO_2\bullet^-$ for addition to the thiocarbonyl group. Studies with deuteriated solvents and reagents indicate that HCO_2^-, not the solvent dimethylformamide, is the major *H*-donor. Secondary

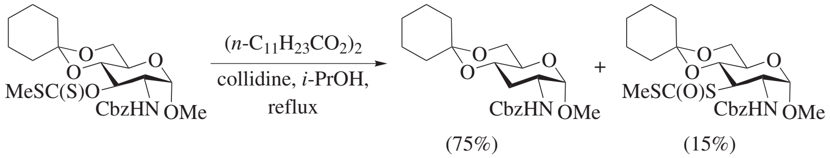
S-methyl xanthates and other *O*-thioacyl derivatives are reduced in 75–100% yields. An example with a substrate containing a free carboxylic acid is shown in Eq. 63.[211]



(Eq. 63)

Because bisulfate is generated during the reaction, $NaHCO_3$ or Na_2CO_3 is included for acid-sensitive substrates. Minor substrate limitations to this system are imposed by the relatively weak hydrogen-donating ability of formate ion and the oxidizing power of persulfate. For example, reduction of *O*-benzhydryl-*S*-methyl xanthate gives the radical dimer, 1,1,2,2-tetraphenylethane, and reductions of 2-arylethanol derivatives yield styrenes.

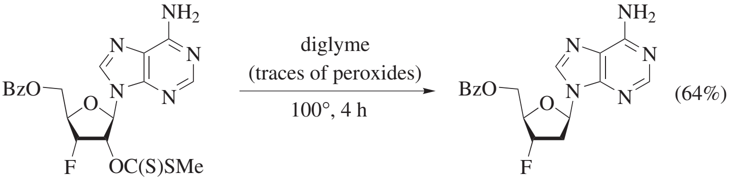
For substrates that bear electron-withdrawing groups (OH, OR, OCOR, F) close to the radical center, the method of Quiclet-Sire and Zard[32] offers mild conditions and inexpensive reagents. The *H*-donor/solvent is 2-propanol, and the (stoichiometric) radical source is lauroyl peroxide [$(n\text{-}C_{11}H_{23}CO_2)_2$]. Collidine is included to buffer any lauric acid produced from the peroxide. An example is shown in Eq. 64,[32] and a cyclitol example is found in the "Applications to Synthesis" section (Eq. 100).



(Eq. 64)

This result is understandable in terms of the effects of radical polarization discussed earlier. Electron-rich 1-undecyl radicals from the peroxide prefer to add to the thiocarbonyl group rather than abstract hydrogen from 2-propanol. Subsequent fragmentation of the adduct generates the relatively electron-deficient, secondary, carbon-centered radical, which abstracts a hydrogen atom from the solvent in competition with adding to the thiocarbonyl group. The latter pathway accounts for the rearranged byproduct. The amount of the dithiocarbonate produced is both substrate- and concentration-dependent. For less polarized radicals, more rearranged material is obtained under the same conditions. For all substrates, the rearrangement becomes the major process in non-*H*-donor solvents such as benzene and affords a free-radical route for replacing a C–O bond with a C–S bond.

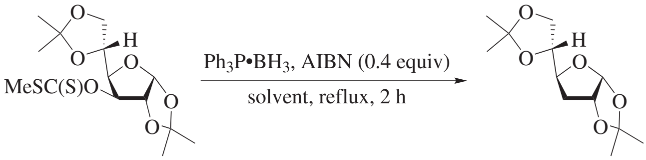
A method related to the foregoing one, but more restricted in substrate class, involves simply heating an *S*-methyl xanthate in bis(2-methoxyethyl)ether (diglyme).[212] Small amounts of peroxides in the diglyme are necessary. Experiments with deuteriated substrates confirm that diglyme is the *H*-donor. All of the examples involve nucleosides, and the presence of a fluoro substituent β to the radical center is essential for obtaining significant amounts of the deoxygenated product. Deoxygenation at either the C2 or C3 position is attained with appropriate substrates (Eq. 65).



(Eq. 65)

Other ethers give lower yields, even with added peroxide initiators. Direct comparisons of these diglyme reactions with the lauroyl peroxide-2-propanol method indicate more reliable results from the latter, over the full range of substrates.

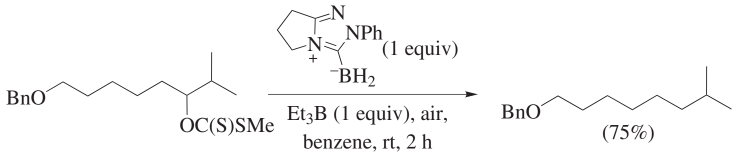
Reductions with Reagents Containing B–H and O–H Bonds. A systematic study[110] of phosphine boranes $R_3P{\bullet}BH_3$ establishes the order of reactivity and solvent effects for the reduction of a standard substrate. In dioxane at reflux, gradually introducing 0.2–0.4 equivalents of AIBN, the order of reactivity for the reducing agents is $Bu_3P{\bullet}BH_3 > Ph_3P{\bullet}BH_3 \sim (TMSO)_3P{\bullet}BH_3 >> (MeO)_3P{\bullet}BH_3$ and $(Et_2N)_3P{\bullet}BH_3$. High yields are obtained with the first three reagents. In benzene, the conversion is diminished for $Ph_3P{\bullet}BH_3$ (Eq. 66)[110] but not for $Bu_3P{\bullet}BH_3$. The co-product in a reduction using the latter reagent is spectroscopically identified as $Bu_3P{\bullet}BH_2SC(O)SMe$. The complex with the silyl phosphite would seem to offer simplicity of work-up, as hydrolysis will form water- and base-soluble species plus volatile hexamethyldisiloxane.



Solvent	Yield (%)
dioxane	90
benzene	42

(Eq. 66)

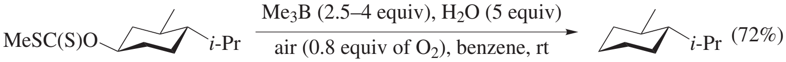
One important point regarding these reagents is that they, together with the O–H based system discussed below, may be the safest choice for reducing substrates containing carbon-halogen bonds. When reactions are run in the presence of various halides, aliphatic iodo compounds are competitively reduced, but no reduction of chloro- or bromo- compounds including 1-bromoadamantane is seen under conditions where the xanthate substrate is fully reduced. Similar reductions have been achieved using borane complexes of aromatic, *N*-heterocyclic carbenes (Eq. 67)[213] and the normal, radical mechanism has been confirmed.[214]



(Eq. 67)

Selectivity for deoxygenation in reactions with substrates containing carbonyl groups is not known for either of these classes of borane complex.

An observation by Wood and co-workers has afforded a novel system ($R_3B{-}O_2{-}H_2O$) based on an O−H donor. *O*-Thioacyl compounds are deoxygenated by a trialkylborane and water in benzene (Eq. 68).[38] Trimethylborane (2.5−5.0 equivalents) is typically employed, although Et_3B and Bu_3B are also used. Complexation of H_2O to a trialkylborane drastically reduces the strength of the O−H bond from 116 kcal/mol (in H_2O) to 86 kcal/mol (in $Me_3B{\bullet}OH_2$), bringing the energy into the donor range suitable for deoxygenations.



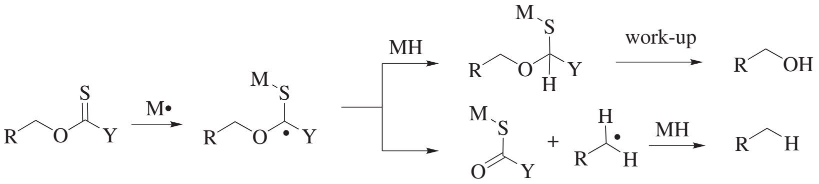
(Eq. 68)

Co-product identification and deuteriation experiments confirm that alkyl radicals generated from R_3B add to the thiocarbonyl group, and that the $R_3B{\bullet}OH_2$ complex is the *H*-donor. Yields are diminished by the presence of competitive Lewis bases.[215] The $R_3B{-}H_2O{-}O_2$ combination reduces aliphatic iodo compounds, but iodo arenes and various chloro- and bromo-compounds, including a benzylic chloride, are recovered unchanged.[111]

Preparative and mechanistic studies[216,217] of the reactions of a range of xanthates with an excess of Et_3B and O_2 in diverse solvents has established that, whereas xanthates of the type *sec*-RSC(S)OEt are cleanly reduced to *sec*-RH, i.e. with C−S scission, deoxygenations of *sec*-$ROCS_2Me$ species typically give complex mixtures. Carefully controlled introduction of O_2 and substrate under high dilution affords moderate to good yields in reductions of the 3-OC(S)SMe and 3-OC(S)Im derivatives of diisopropylidene-α-D-glucofuranose.[216] In these reductions, both O−H and C−H donor species (adventitious, complexed H_2O or ROH; solvent; Et_3B) are involved.[217]

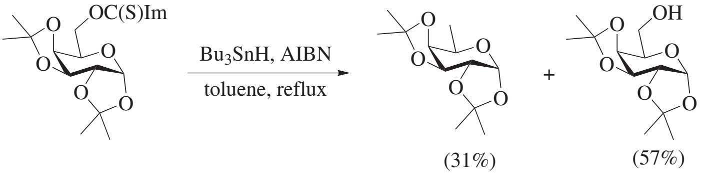
Primary Alcohol Derivatives

As mentioned in the "Mechanism and Stereochemistry" section, the choice of the combination of thioacyl derivative, the reducing system, and the reaction conditions are more important for primary than for secondary substrates. The higher energy of the primary radical slows the fragmentation step and can thus favor the reduction of the intermediate adduct radical leading to the side-products described earlier, commonly the alcohol (Scheme 8).

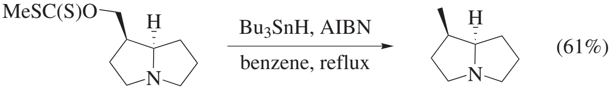


Scheme 8

The initial study[1] explored *O*-thioacyl derivatives of 1-octadecanol, and obtained no significant amount of reduction product from non-initiated reactions with Bu_3SnH run in refluxing toluene. Low yields are obtained under initiated conditions.[30] Arguably, a 1-alkanol derivative affords the most stringent test by providing the lowest level of steric compression in the adduct radical. Indeed, such reactions run on more complex substrates in toluene or even in refluxing benzene afford modest to fair product yields, as illustrated in Eqs. 69[72] and 70.[218] These results are typical for most examples (see Table 1 of the "Tabular Survey") run under the "usual" conditions, although higher yields have occasionally been reported.[219,220]

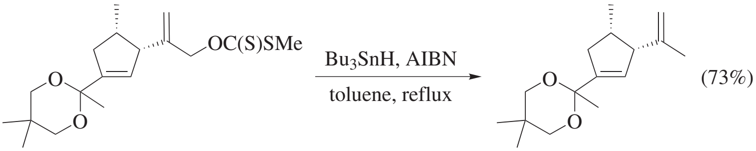


(Eq. 69)



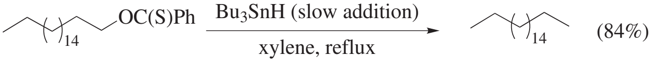
(Eq. 70)

The respectable yields from the lower temperature reaction of Eq. 70 and the reduction shown in Eq. 95 ("Applications to Synthesis" section) reflect steric effects that encourage the fragmentation of the bulky adduct radical located on the concave face of a bicyclic system. As expected, radical stabilization through allylic or benzylic conjugation also improves yields (Eq. 71).[221]



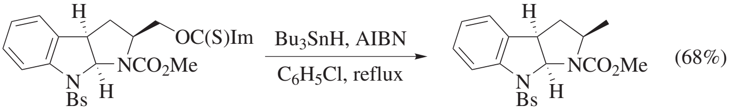
(Eq. 71)

More systematic studies have established reliable conditions for the efficient reduction of all types of primary alcohol derivatives using combinations of the obvious choices from Scheme 8 that might favor fragmentation over *H*-capture for the initial radical; for example, changing the temperature and dilution, the nature of Y, and the reducing agent. By simple modifications to the original conditions, namely changing to the counter-intuitive slow addition of Bu_3SnH to the substrate (initial concentration = 0.05–0.2 M) at higher temperatures, greatly improved yields are obtained. The formation of thioester by the reaction of the intermediate alkyl radicals with the substrate is not an issue. *S*-Methyl xanthates are best reduced in *p*-cymene at 160°; xylene at 130–140° is used for *O*-thiobenzoyl and *O*-(imidazol-1-ylthiocarbonyl) derivatives (Eq. 72).[59]



(Eq. 72)

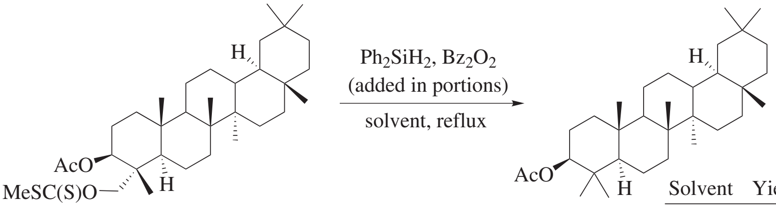
Chlorobenzene is also a suitable solvent (Eq. 73).[222] The reduction of a primary thiocarbonate of the type $R^1CH_2OC(S)OCH_2R^2$ at 160° was shown in Eq. 7 in the "Mechanism and Stereochemistry" section.[30]



(Eq. 73)

Using *O*-(2,4,6-trichlorophenyl)- or *O*-(pentafluorophenyl) thiocarbonates, high-yielding reductions at somewhat lower temperatures are achieved.[35] This result reflects the facilitation of the fragmentation step for primary substrates, since competition experiments between *sec*-ROC(S)Y species show that the relative rates of consumption of these substrates vary by a factor of only 4 with the order of reactivity: Y = SMe > OC_6H_5 > OC_6F_5.[69]

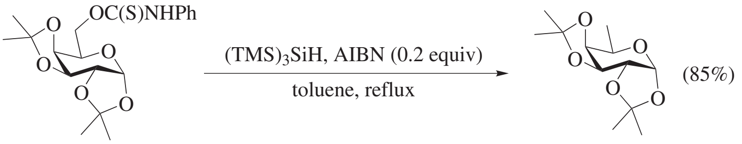
Reducing the efficiency of the *H*-donor can also improve yields in deoxygenations of primary alcohol derivatives, although benzylic derivatives can give the radical dimer as a coproduct.[75] With the caveat that the gradual addition of up to 1.5 equivalents of an initiator may be required to compensate for short-chain lengths, good yields are obtained from reductions with Et_3SiH,[75,171] $PhSiH_3$,[35,172] and Ph_2SiH_2 or Ph_3SiH.[35] Again, higher temperatures than those used for secondary derivatives are beneficial (Eq. 74).[35]



Solvent	Yield (%)
toluene	56
xylene	75

(Eq. 74)

An alternative mode for continual initiation uses the Et_3B-O_2 system, gradually introducing O_2 in the form of air. Although this technique affords poor yields with primary substrates under the conditions used to effectively reduce secondary ones (room temperature, Bu_3SnH),[91] good results are obtained in refluxing benzene with Ph_2SiH_2.[173] The longer chain lengths attained with $(TMS)_3SiH$ permit reductions that do not require the gradual addition of initiator.[30,39] An example is shown in Eq. 75.[39]



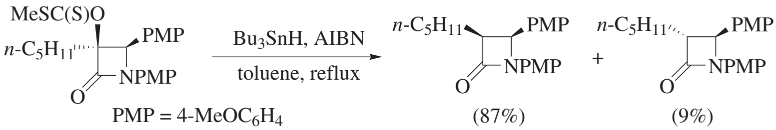
(Eq. 75)

The polarity reversal method using Et_3SiH with catalytic amounts of an initiator and $t\text{-}C_{12}H_{25}SH$ reduces primary *S*-methyl xanthates in acceptable yield,[175,223] and most of the P–H reagents discussed in the context of secondary alcohol derivatives have also been used for primary alcohol deoxygenations.[112,193,194,205,206]

With respect to O–H and C–H donors, a room-temperature reduction of a primary substrate achieved in 42% yield using the $Me_3B-H_2O-O_2$ system[38] suggests the possibility of improved yields at higher temperatures with this reagent combination, and reductions of primary *S*-methyl xanthates using the formate–persulfate system afford excellent yields of the deoxygenated product,[211] although a similar reduction of a primary ROC(S)Im derivative is less efficient.[224]

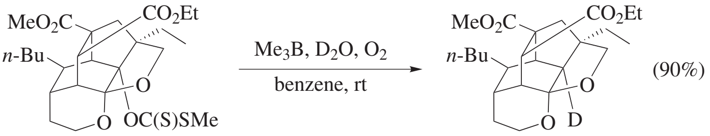
Tertiary Alcohol Derivatives

Tertiary *O*-thioacyl derivatives that are not prone to cyclic elimination pose no problems and are efficiently deoxygenated under any of the standard conditions. An example on a β-lactam ring is shown in Eq. 76.[225] Other examples were shown in the "Mechanism and Stereochemistry" section (Eqs. 8–10).



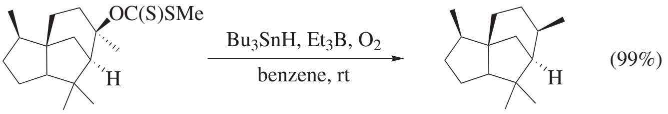
(Eq. 76)

Excellent yields are also obtained with the $Me_3B-H_2O-O_2$ system where D_2O is used to introduce deuterium (Eq. 77).[38]



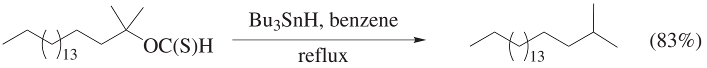
(Eq. 77)

If the xanthate is stable at room temperature but decomposes on heating, the Et_3B-O_2 initiation system is used (Eq. 78).[81]



(Eq. 78)

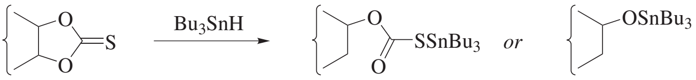
When the ease of elimination precludes the formation of a xanthate or *O*-(phenoxythiocarbonyl) derivative the corresponding *O*-thioformate, prepared under the neutral conditions described earlier, is used. Although thioformates of non-hindered alcohols are poor deoxygenation substrates because of preferential reduction over fragmentation of the adduct radical, the combination of tertiary radical stability and steric compression accelerates the fragmentation for the tertiary derivatives (Eq. 79).[33]



(Eq. 79)

Cyclic Thiocarbonates

O,*O*-Thiocarbonyl derivatives of diols (cyclic thiocarbonates), usually with 5- or 6-membered rings, are reduced under the same conditions as other *O*-thioacyl compounds. Representatives from most of the classes of reducing agents described in the foregoing sections have been successfully employed. The structure of the initial product in reductions using Bu_3SnH (Eq. 80) has not been determined, but loss of COS from **65** to give the stannyl ether **66** is likely, by analogy with the reductions of xanthates and phenoxythiocarbonates discussed in the "Mechanism and Stereochemistry" section. However, as noted earlier, the isolation of the bis-deoxygenated compound as the major product in a reduction of a thiocarbonate with excess Ph_3SiH indicates that the triphenylsilyl analog of **65** is more stable.[36]

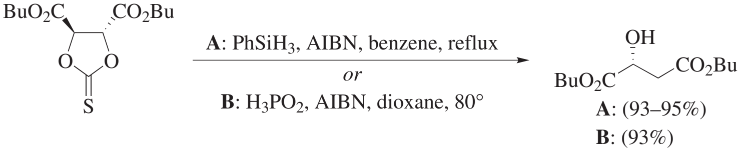


65 **66**

(Eq. 80)

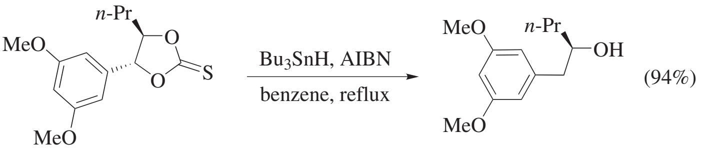
The original description of the reaction[85] included a hydrolysis step using aqueous sodium hydroxide. This step removes *O*-acyl groups and will clearly pose a problem for any other base-sensitive entities in a target molecule. However, this step is apparently not essential, as other reductions have retained the acyl groups by chromatographic purification of the crude product either directly or following a simple, partitioning work-up.

Although Bu_3SnH is most frequently employed, successful thiocarbonate deoxygenations also use Ph_3SnH, silane reagents, H_3PO_2, and the formate-persulfate system. With respect to effects of the choice of reagent on yields, few direct comparisons are available. The results shown in Eq. 81 indicate that silanes[226] and H_3PO_2[227] are equivalent.



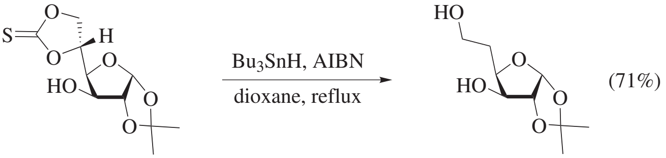
(Eq. 81)

Eq. 82 shows a typical reduction using Bu_3SnH. The direction of bond scission is determined by the formation of a stabilized, benzylic radical.[228]

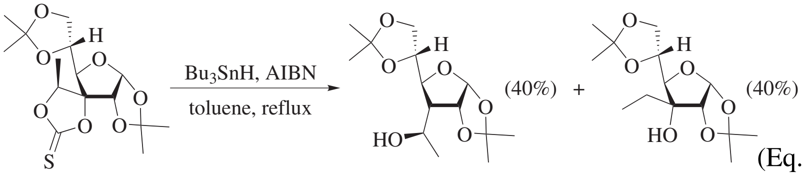


(Eq. 82)

In general, when a conjugated radical can be formed, this factor dominates the direction of fragmentation (and hence, the site of reduction) for both 5- and 6-membered ring substrates. Other examples include a propargylic system[229] and a reduction at a benzylic center in preference to a tertiary center.[230] However, the situation is more complex for thiocarbonates in which the only radical-stabilizing factor is the degree of alkyl-type substitution. Simple, 5-membered ring systems typically follow classical radical stability rules, as in the example of secondary vs. primary in Eq. 83,[231] but increasing levels of substitution lead to loss of selectivity in a secondary vs. tertiary case (Eq. 84).[232]

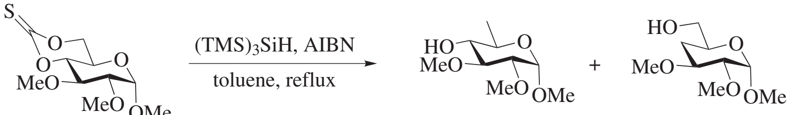


(Eq. 83)



(Eq. 84)

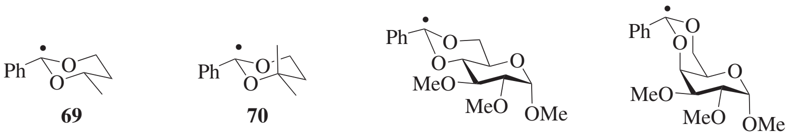
As expected, discrimination between the two secondary positions in 2′,3′-thiocarbonates of nucleosides and other furanosides is poor.[85,233,234] In the absence of radical stabilization by conjugation, the site selectivity of reduction of 6-membered ring thiocarbonates is not intuitive. The initial observation[85] of reduction at the secondary position in a 4,6-*O*,*O*-(thiocarbonyl)glucopyranoside derivative was subsequently shown to be in error, due to an incorrect product structure assignment; in fact, fragmentation favors the formation of the primary radical as shown by the predominance of product **67** over **68** in Eq. 85.[36] Other reducing agents give similar ratios.



67 **67**:**68** = 92:8 **68**

(Eq. 85)

These observations correlate with results from the fragmentations of 2-phenyl-2-dioxanyl radicals into the corresponding γ-benzoyloxy radicals[36,235] (Fig. 3). The “acyclic” cases **69** and **70** favor the more substituted radicals, whereas the glucopyranoside case **71** again gives mostly the primary radical, and the galactopyranoside analog **72** exhibits moderate selectivity for the secondary direction.



69
1°:2° = 13:87

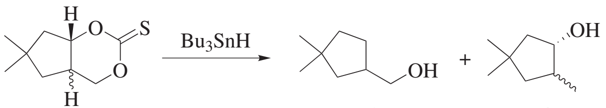
70
1°:3° = 1:99

71
1°:2° = 97:3

72
1°:2° = 38:62

Figure 3. Fragmentation of 2-phenyl-1,3-dioxan-2-yl radicals.

Reduction by the formate–persulfate system at the primary center in a 6-membered ring thiocarbonate in a furanoside has also been observed.[211] The distribution of products **73** and **74** in Eq. 86 shows that this apparently contra-thermodynamic ring opening is not unique to carbohydrate substrates (Eq. 86).[84] In this simple system the ring fusion again determines the product distribution, and the *trans*-configured starting material undergoes mostly primary C–O bond scission. Similar results are found with cyclic acetals derived from *cis*- and *trans*-2-hydroxy-1-cyclohexanemethanol.[236]



cis or *trans* **73** **74** *cis* or *trans*

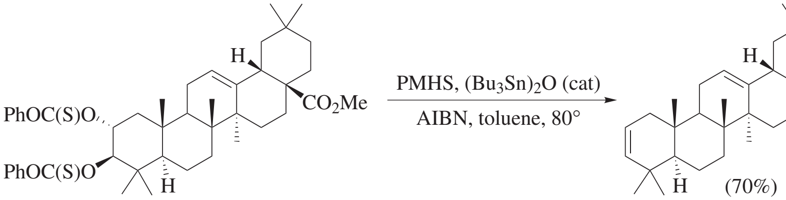
cis **73**:**74** = 19:1
trans **73**:**74** = 1:21 (Eq. 86)

Molecular mechanics calculations for the radical fragmentation step in both of these systems[36,84,236] confirm the observed outcomes. Minimized transition states for the *cis*-fused bicyclic systems resemble those for the monocyclic systems, and the formation of the more stable secondary radical is favored. In contrast, energy minimization for the *trans*-fused systems predict that lengthening the primary C–O bond presents the lower-energy pathway, even though the resulting radical is less stable than its secondary isomer.

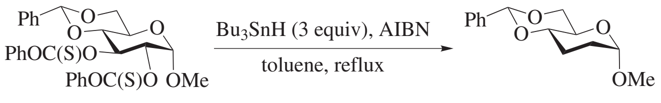
Thiocarbonate reductions show side-product profiles similar to those seen in other deoxygenations, and the ratio of desired to undesired pathways is solvent-dependent in one case.[237] Reduction of the thiocarbonyl group to a methylene group is observed in some reactions using Bu_3SnH[36] and is the major path in one example using Ph_3SnH.[143] Replacing the stannane with $(TMS)_3SiH$ or Ph_3SiH alleviates the problem in the first case. Reductions with Bu_3SnH of the structurally related 1,3-oxathiolane-2-thiones (cyclic xanthates) bearing a single substituent adjacent to the endocyclic sulfur give mixtures of the corresponding olefin plus the 1,3-oxathiolane, with the latter favored by high concentrations of the reducing agent.[238]

1,2-Bis(*O*-Thioacyl) Derivatives

The conversion of 1,2-diols via their bis(xanthates) to alkenes with Bu_3SnH[239] offers the advantage of a neutral, two-step method that is insensitive to the configuration of the starting diol. The best substrates appear to be *S*-methyl xanthates, which constitute the majority of the examples, or *N*-phenylthiocarbamates.[88] Thiobenzoates are not suitable substrates, because the adjacent thiocarbonyl group preferentially traps the radical that is formed by the initial addition-fragmentation process.[1] 1,2-(Bis)xanthates do not usually react in this manner, although one example is known[240] in a reaction carried out at 80°. A similar process has been recorded for a bis(xanthate) of a 1,3-diol.[30] Only rigid, *trans*-diols that cannot form cyclic thiocarbonates can be converted into 1,2-bis(OC(S)Im) compounds. Upon reduction one such example affords a mixture of the alkene and the bis(deoxy) compound.[241] With 1,2-bis(OC(S)OPh) derivatives, the product distribution depends upon the conditions, especially the concentration of Bu_3SnH. With a steroidal substrate and a catalytic tin system, the alkene is obtained (Eq. 87),[242] whereas a carbohydrate derivative affords the bis(deoxy) compound when combined with an excess of Bu_3SnH (Eq. 88).[67] A similar result is reported for a 5-membered ring system.[243]

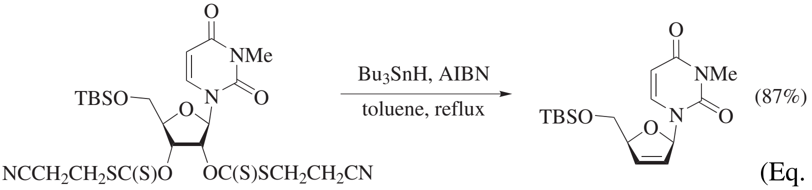


(70%) (Eq. 87)

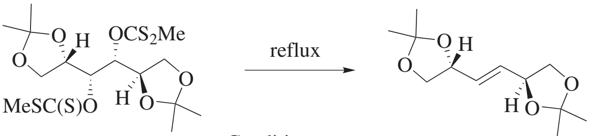


(66%) (Eq. 88)

No saturated products have been reported from reductions of bis(xanthates), indicating that the β-elimination step is more facile for these derivatives than for their phenoxy analogs. An important application of this reaction is the synthesis of antiviral 2,3-dideoxy-2,3-didehydro nucleosides, which are readily obtained from Bu_3SnH reductions of bis(*S*-methyl) xanthates[86,239] and the corresponding *S*-(2-cyanoethyl) compounds (Eq. 89).[86]


(Eq. 89)

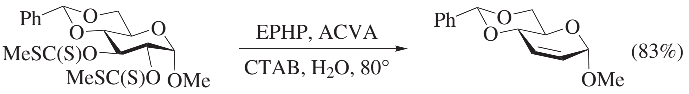
Reductions using silanes[244] are also effective. On the basis of a limited number of direct comparisons with stannane reductions, they tend to afford improvements in yield (Eq. 90). As is known for other ROC(S)Y derivatives, the reductions using simple silanes require portionwise addition of one equivalent or more of the initiator. No addition of the reagent to the product alkene is seen with silanes or stannanes.



Conditions	Yield (%)
Bu_3SnH, AIBN, toluene	65
Et_3SiH (neat), Bz_2O_2	82
Ph_2SiH_2, AIBN, toluene	92

(Eq. 90)

Efficient alkene formation is also attained using P–H based reagents. An example using an aqueous hypophosphite system with a phase-transfer agent is shown in Eq. 91.[199] The yield is superior to that reported for the Bu_3SnH reduction of the same substrate,[239] although a near-quantitative yield is reported with a polymer-bound stannane.[104]

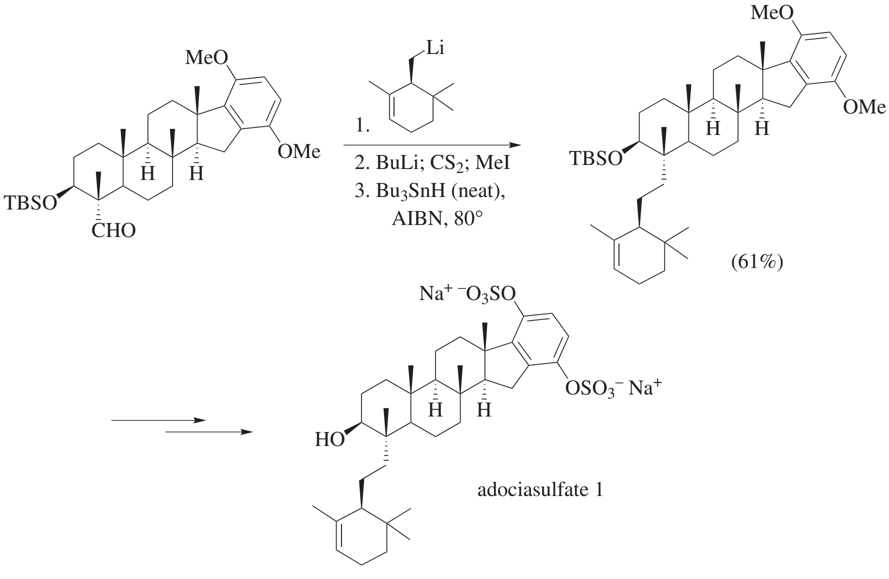

(Eq. 91)

Reductions using dialkyl phosphites or H_3PO_2 salts in organic solvents can lead to the addition of the reagent to the product alkene. Including a sacrificial alkene such as 1-dodecene in the reaction can minimize this process.[194]

APPLICATIONS TO SYNTHESIS

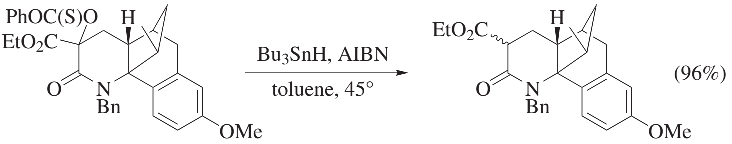
Total Synthesis

The neutral reaction conditions and the high degree of tolerance to steric environments and functional groups have resulted in the use of free-radical deoxygenation in the total syntheses of complex molecules, where the route has required that an oxidized carbon be either carried through to, or introduced at, a late stage and then reduced. Key, late steps in the synthesis of the kinesin inhibitor adociasulfate 1, where a connective sequence uses an organolithium addition followed by a deoxygenation, are shown in Scheme 9.[245]



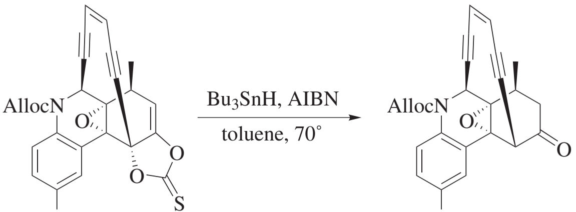
Scheme 9

Alkaloid syntheses have also employed deoxygenations, as exemplified by a step in a synthesis of a key intermediate for lycopodine (Eq. 92).[246]



(Eq. 92)

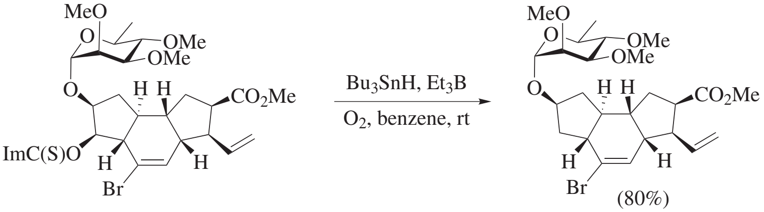
An interesting reduction of a cyclic ene-thiocarbonate, employed during a synthesis of dynemicin A and structural analogs, is shown in Eq. 93. Selectivity is secured by virtue of the high energy of the vinyl radical that would result from the alternative fragmentation and by the bridgehead structure, which prevents the fragmentation of the oxirane ring adjacent to a radical.[247,248]



R	Yield (%)
Me	60
TBS	97

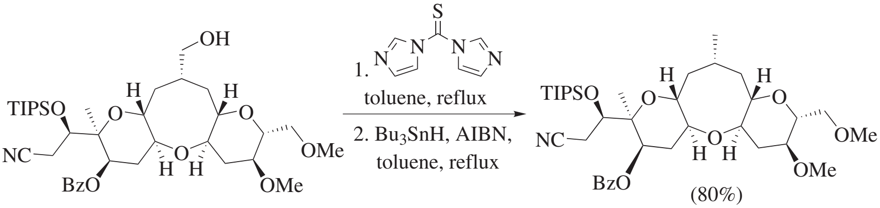
(Eq. 93)

Functional-group selectivity is demonstrated in a reductive step in the synthesis of the potent insecticide spinosyn A, in which a bromoalkene and a terminal double bond survive the deoxygenation step (Eq. 94).[249] A reduction of a similar structure with $(TMS)_3SiH$ at 80° results in debromination.[250]



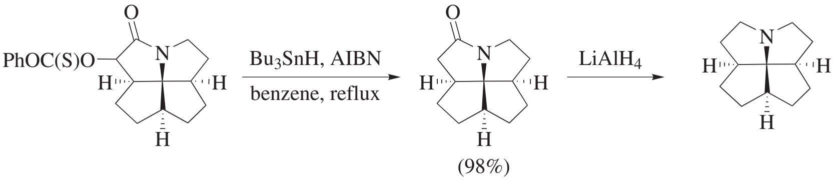
(Eq. 94)

Synthetic efforts in the marine polyether area (ladder toxins) have also included free-radical deoxygenations.[220,251–254] Eq. 95 shows the removal of a primary hydroxyl in a synthesis of the HIJ framework of ciguatoxin.[220]



(Eq. 95)

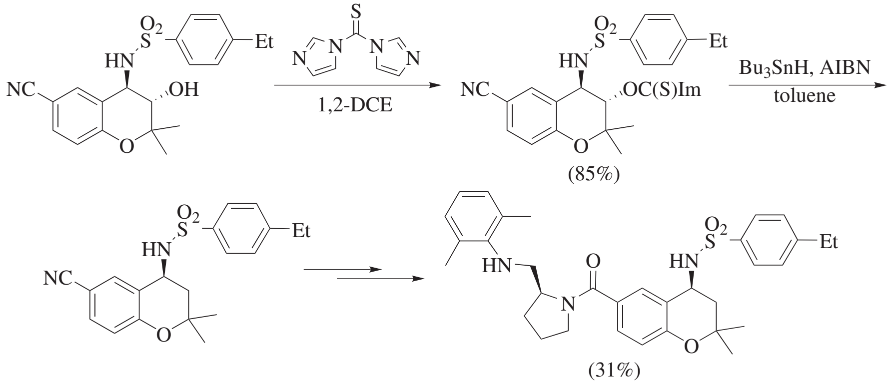
Syntheses of non-natural products with interesting molecular architecture or biological activity have also employed the reaction. Examples of the former include the penultimate step in the synthesis of an azafenestrane (Scheme 10),[255,256] and the preparation of a series of stereochemically defined oligocyclopentanes.[257]



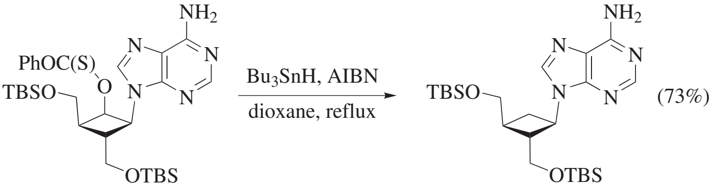
Scheme 10

The removal of a hindered, secondary hydroxyl during the synthesis of a potassium channel antagonist is shown in Scheme 11.[258]

Deoxygenations are also found in several syntheses of carbocyclic nucleosides, including the carba analogs of 2-deoxythymine,[259,260] 2-deoxyadenosine,[261] and oxetanocin.[262] The latter is shown in Eq. 96.

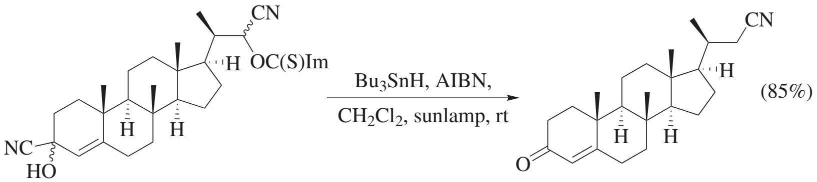


Scheme 11



(Eq. 96)

A method for homologating aldehydes into nitriles, employed in both synthesis and natural product modification, involves conversion to the cyanohydrin (using Et_2AlCN) followed by deoxygenation of the –OC(S)Im derivative.[27] When the starting material contains a ketone, this also forms the corresponding cyanohydrin, but the resulting tertiary hydroxyl is not thioacylated by TCDI. In the reductive step, the ketone is then regenerated in a process shown to be mediated by the co-product, Bu_3SnIm (Eq. 97). The reduction conditions are somewhat unusual, employing both an initiator and visible light irradiation at room temperature.

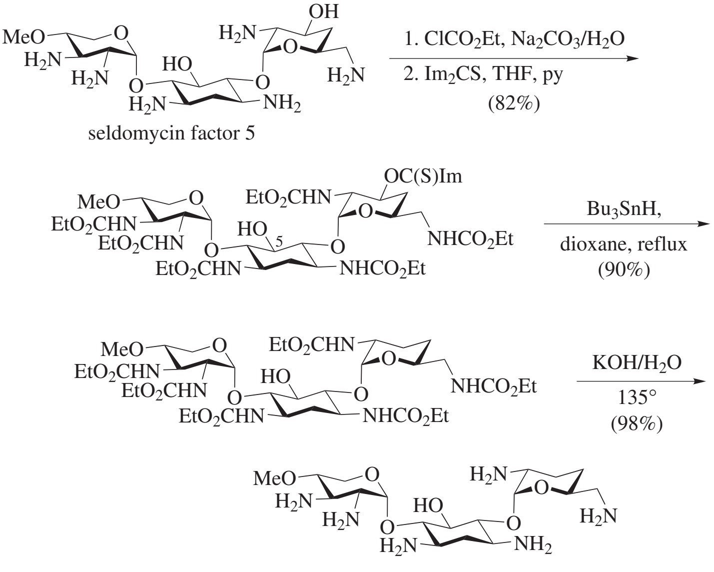


(Eq. 97)

Modification of Natural Products

Conceived originally as a method for the selective removal of hydroxyl groups in densely functionalized antibacterial agents, notably aminoglycosides and macrolides, the reaction has been used not only for that purpose but also for modifying a wide variety of other naturally occurring molecules. A mono-deoxygenation in an aminoglycoside derivative, used for the preparation of

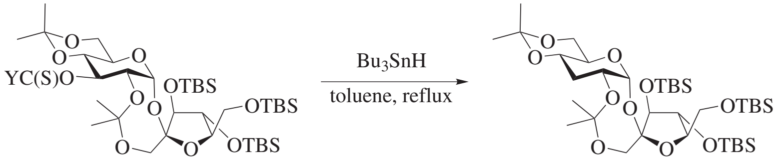
3′-deoxyseldomycin factor 5, is shown in Scheme 12. The hindered 5-OH on the central deoxystreptamine ring does not react with Im_2CS in the thioacylation step,[263] but can be removed from related substrates via the *O*-thioformate.[264]



Scheme 12

A similar reduction of a tris(xanthate) in a kanamycin derivative allows simultaneous deoxygenation and alkene formation.[61] The deoxygenation of macrolide derivatives with P–H reagents[197,203] was discussed in the "Scope and Limitations" section (see Eq. 60). Stannanes have also been used for this purpose.[265] The reaction has found substantial application in the taxane area: Eq. 22 in the thioacylation section showed the preparation of an *O*-(pentafluorophenoxythiocarbonyl) derivative, and this is reduced very efficiently.[70] Similar chemistry at other positions in taxanes may be complicated by skeletal rearrangements, as discussed earlier.[143] Other applications of free-radical deoxygenations to complex, polycyclic natural products include: a key step in the conversion of diosgenin to (25*R*)-26-hydroxycholesterol;[266] modification of the anti-parasitic avermectins;[267] and reductions at various sites in alkaloids of the aconitine family.[268] Indolocarbazoles related to the potent kinase inhibitor staurosporin have been modified through cyclic thiocarbonates,[269] and deoxygenations of –OC(S)Im derivatives of the tricothecane toxins have been reported.[241,270–272] Earlier sections have exemplified the extensive use of free-radical reductions of nucleosides.

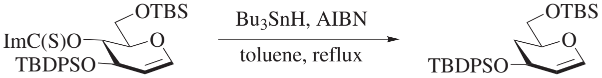
Reductive modifications of carbohydrates can be used to alter the natural product as an end in itself; Eq. 98 shows the synthesis of a protected 3-deoxysucrose.[273,274]



(Eq. 98)

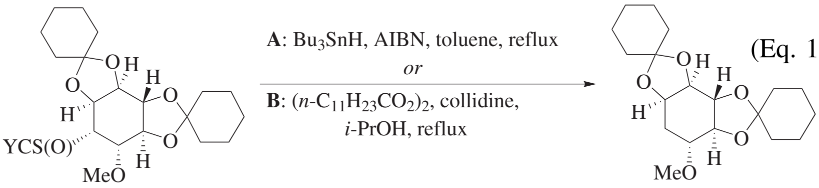
Y	Yield (%)
Im	76
MeS	93

In addition, carbohydrate deoxygenations are frequently used to obtain key intermediates from the “chiral pool” for the synthesis of more complex substances. The preparation of a 4-deoxy-D-glucal derivative (Eq. 99) is representative.[275,276]



(85%) (Eq. 99)

Deoxygenations of cyclitols are also conveniently carried out by free-radical methods. Eq. 100 shows two sets of conditions used to reduce *O*-thioacyl-*myo*-inositol derivatives.[32,277]



(Eq. 100)

	Y	Yield (%)
A:	Im	74
B:	MeS	90

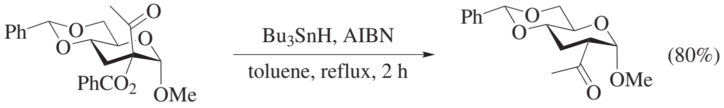
COMPARISON WITH OTHER METHODS

This section exemplifies and discusses alternative methods for deoxygenating alcohols and for converting 1,2-diols into alkenes, and is subdivided according to the nature of the process or the species which is undergoing reduction. The major focus is on those methods that involve hydroxyl group functionalization followed by direct, reductive cleavage of the carbon-oxygen bond. More limited coverage is accorded to stepwise processes that involve the replacement of the C–O bond (e.g. by C–halogen or C–S) followed by a separate reduction step, and to the special options available for reducing allylic and benzylic alcohols and their ethers and esters.

Deoxygenations

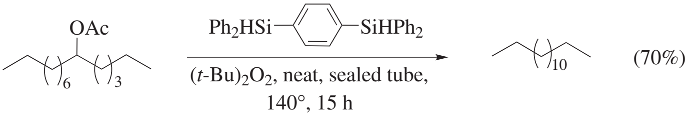
Methods Involving C–O Homolysis Followed by Hydrogen Atom Abstraction. Both thermal and photochemical methods are available for these processes.

Reduction of Esters. The direct deoxygenation of simple benzoates by Bu_3SnH[278] is feasible only when a highly stabilized radical is formed, and is not of general applicability. These reactions may involve S_H2 attack on the ethereal oxygen of the ester. α-(Benzoyloxy) ketones are more easily reduced, especially when the intermediate radical is tertiary (Eq. 101).[279]



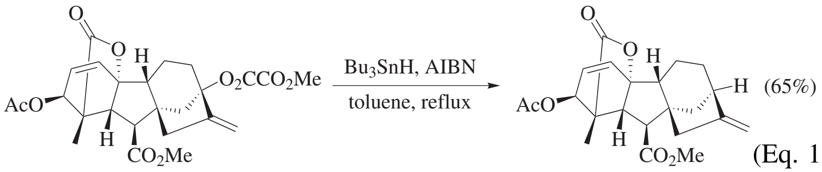
(Eq. 101)

Acetates of simple alcohols are reduced to the hydrocarbon by heating at 140° without solvent in a sealed tube with $(t\text{-Bu})_2O_2$ and an excess of either Ph_3SiH[280] or the readily prepared bis(silane) shown in Eq. 102.[281] 1,2-Diacetoxycyclododecane affords the saturated hydrocarbon, but no applications to more complex substrates are reported. Reduction of ketone carbonyl groups and *C*-halogen bonds, and hydrosilylation of olefins and acetylenes, is to be expected under these conditions.



(Eq. 102)

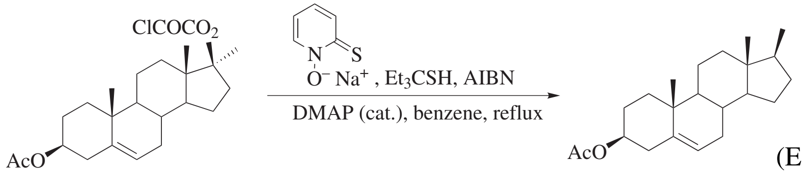
Milder conditions are available using oxalate-functionalized substrates. Bu_3SnH reductions of methyl oxalate esters of tertiary and hindered secondary alcohols can afford good yields of deoxygenated product (Eq. 103).[282] This method has been used in the synthesis of bilabolide[283] and for modifying anisatin.[284] The powerful acylating capabilities of methyl oxalyl chloride make this method attractive for such substrates, but for primary and non-hindered secondary substrates the starting alcohol is frequently the major product of the reduction step.



(Eq. 103)

The mechanism of this reaction is assumed to involve reversible addition to the oxalate carbonyls, with C–O fragmentation occurring when a favorable substitution pattern is available, but the details are not known. More is known concerning a process for deoxygenating tertiary alcohols, wherein the substrate is a mixed oxalic ester with 1-hydroxy-1,2-dihydropyridine-2-thione.[285] This method is a special case of the generation of acyloxy radicals from *O*-acyl thiohydroxamates, a general process for the free-radical decarboxylation of carboxylic acids.[286]

As Eq. 104 shows, the optimum reducing agent is a hindered thiol and the mixed ester is generated in situ.[285]

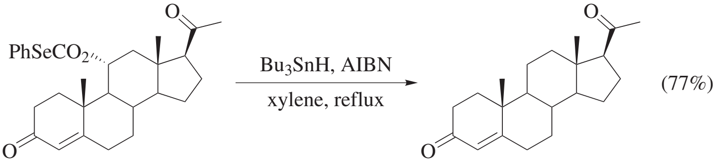


(77%)

(Eq. 104)

When applied to chloroglyoxylates of secondary alcohols, this method gives only the formate ester even at 178°, indicating that loss of one molecule of CO_2 is followed by hydrogen donation from the thiol to the resulting alkoxycarbonyl radical. In the tertiary system the second decarboxylation clearly precedes hydrogen abstraction, if the same stepwise mechanism operates.

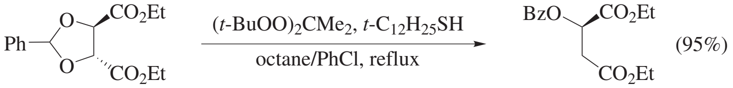
Reduction of Chloroformates and Related Species. The thermal instability of chloroformates restricts their use in deoxygenation processes, although structurally simple, saturated, primary and secondary substrates are reduced in neat n-Pr_3SiH with t-Bu_2O_2 at 140°.[287] The analogous Bu_3SnH reduction of phenylselenoformates, which are prepared by reacting chloroformates with benzeneselenol (PhSeH), is a more general process: the facility of the S_H2 attack of stannyl radicals on selenium allows rapid reactions using catalytic initiator in dilute solution. Temperatures of 140–150° are needed to ensure decarboxylation before hydrogen capture. Eq. 105 illustrates that ketones are unaffected.[126]



(Eq. 105)

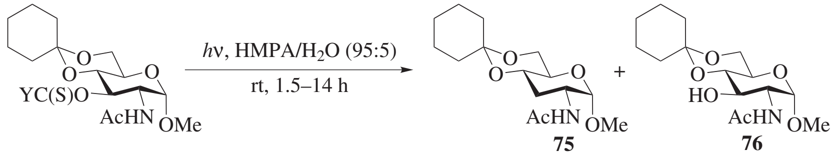
The analogous primary derivatives are reduced at higher temperatures; tertiary derivatives are reduced easily, but can be made only in poor yield. Disadvantages of this method are the need to prepare the chloroformate, and the noxious and toxic nature of PhSeH. Other reducing agents have not been applied to these substrates.

Abstraction-Fragmentation from Acetals. The site selectivity of this fragmentation process was discussed earlier in the context of the reduction of cyclic thiocarbonates (Eq. 5). For suitable substrates, this is a useful, catalytic method for monodeoxygenation of 1,2- and 1,3-diols, with the obvious proviso that the acetal hydrogen must be the most easily abstracted one in the substrate molecule. The polarity reversal method using 0.05 equivalents each of thiol and initiator secures efficient conversions (Eq. 106).[235]



(Eq. 106)

Photochemical Methods. Studies of the visible-light irradiation of *O*-thiobenzoates show that the fully saturated compounds are slowly converted into their *S*-benzoyl isomers [ROC(S)Ph to RSC(O)Ph] via *O*-alkyl bond homolysis followed by recombination within the solvent cage.[288,289] This observation set the stage for non-photochemical exploitation of the driving force of C=O bond formation, including the development of the deoxygenation reaction. Photolysis of homoallylic and similar *O*-thiobenzoates that bear an activated β-hydrogen results in a clean, cyclic elimination of thiobenzoic acid to form the alkene.[288,289] Photolysis of several, carbohydrate-derived ROC(S)Y species in HMPA/H_2O at 254 nm does afford reasonable yields of the deoxygenated product **75**, plus some of the original alcohol **76** (Eq. 107),[290] but the photolysis of steroidal *S*-methyl xanthates in HMPA/H_2O[291] and diverse *O*-(*N*,*N*-dimethylthiocarbamates) in methanol[292] is less efficient.

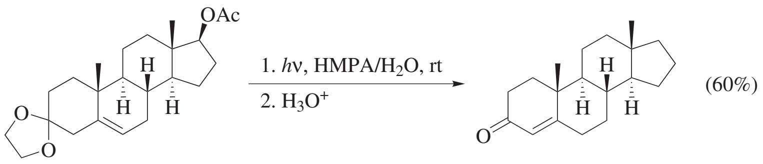


75 **76**

	Yield (%)	
Y	**75**	**76**
MeS	57	12
Im	54	17
Me_2N	52	10

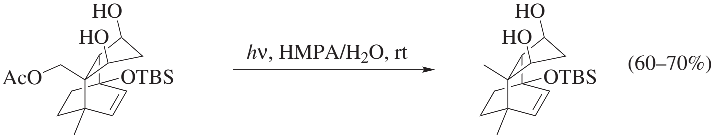
(Eq. 107)

The best substrates for photoreductions are simple esters. In substrates lacking any significant UV absorption, deoxygenations of acetates or pivalates of alcohols are achieved by photolysis at 254 nm in HMPA/H_2O.[290,293–297] These reactions involve light absorption by HMPA, followed by electron donation to the ester, C–O bond homolysis, and finally hydrogen capture from HMPA.[298] Reduction of the intermediate radical to a carbanion is not involved, as β-eliminations of alcohols, ethers, or esters are not encountered. The reaction is prevented by UV-absorbing chromophores in the substrate; for example, testosterone acetate must first be converted to the ketal, which is then reduced and hydrolyzed (Eq. 108).[293]



(Eq. 108)

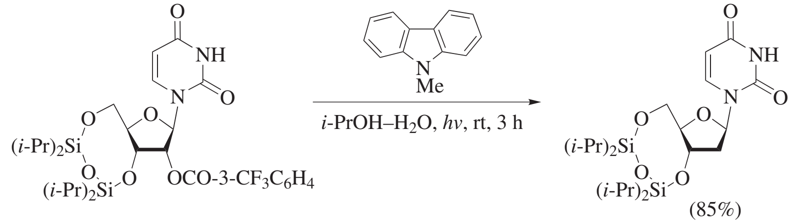
Similar photoreductions of a formate and a benzoate return some of the original alcohol as a co-product.[293] Efficient reductions of secondary and primary acetates at various positions in both furanosides and pyranosides are possible,[295,296] the exception being the anomeric position where only the alcohol is obtained. One instance of an improved yield from a pivalate is known.[296] A reduction at a primary center in a synthesis of trichodermol is shown in Eq. 109.[299]



(Eq. 109)

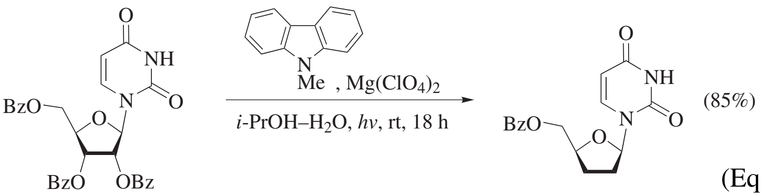
Although methane- and arenesulfonates undergo O–S cleavage to produce the alcohol under these conditions,[290] *O*-trifluoromethanesulfonates (triflates) undergo photoreduction in the same manner as acetates.[300] Chemically, the limitations to these reductions are the need for UV-transparent substrates and the concomitant reduction of ketones and *C*–halogen bonds. A more significant issue is the need to operate in dilute solutions in HMPA, which is a known carcinogen. Multigram reactions can be run with up to 50% H_2O, but HMPA is still the required co-solvent and extended irradiation times are necessary.[296]

The use of HMPA is avoided, and UV absorption by the substrate is tolerated, when sensitized photoreduction is employed. By irradiation through Pyrex in aqueous ethanol or 2-propanol containing one equivalent of 9-methylcarbazole as the sensitizer, efficient reductions of secondary 3-(trifluoromethyl) benzoates are achieved (Eq. 110).[301]



(Eq. 110)

Benzoates may be employed, provided that magnesium perchlorate is also included in the reaction solution. Primary esters are unaffected. A significant difference from Bu_3SnH-thioester reductions is that vicinal diesters produce only the dideoxy compounds, not alkenes (Eq. 111).

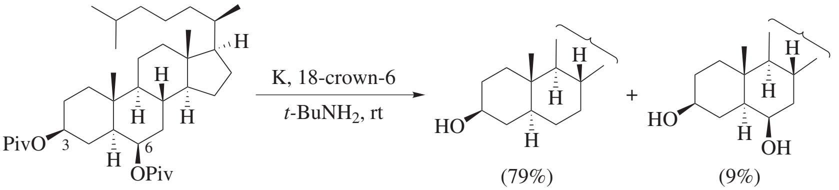


(Eq. 111)

The new proton in the deoxygenated product is derived from the α-proton of the alcohol solvent. A subsequent study shows that 3,6-dimethyl-9-ethylcarbazole can be used as the sensitizer in sub-stoichiometric amounts and that magnesium perchlorate increases the reaction rate for both substituted and unsubstituted benzoate esters.[302]

Methods Involving Carbanion Formation Followed by Protonation. Both dissolving metal and electrochemical modes are available for these deoxygenations, which offer the advantage of simplicity of reagents. Significant substrate limitations arise from the presence of other reducible moieties, including all ketones, conjugated alkenes, allylic, and benzylic *C*-heteroatom bonds, all C–Cl, C–Br, and C–I bonds, sulfoxides, sulfones, and electron-deficient aromatic and heterocyclic rings. Elimination of β-heteroatoms can also take place.

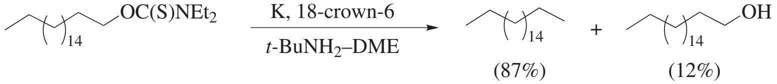
Metal-Amine Reductions of Esters, Phosphoramidates, and Related Substrates. When esters are reduced under conditions in which solvated electrons have reasonable persistence, the C–OCOR bond can undergo scission, with deoxygenation as the net result. Deacylation to form the starting alcohol is a competitive process at relatively non-hindered positions, as shown by the example in Eq. 112, where only the hindered (axial) 6β-pivaloyloxy group is removed.[303] Lithium in ethylamine and potassium plus 18-crown-6 in *tert*-butylamine give similar results.



(Eq. 112)

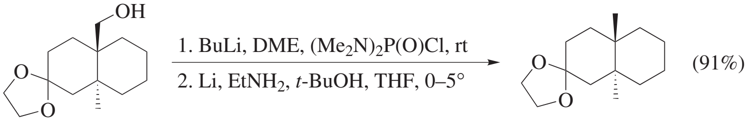
Increased bulk in the carboxylate portion improves the situation for less hindered alcohols, but deacylation cannot be completely suppressed.[304] An alternative to 18-crown-6 for these reductions, tris(3,6-dioxaheptyl)amine [TDA-1; $(MeOCH_2CH_2OCH_2CH_2)_3N$] is effective, and offers the advantages of reduced cost, greater stability towards the metal reagents, and ease of removal.[305] Non-hindered, secondary acetates give the deoxycompound plus the alcohol; reductions of carboxylates derived from hindered acids are not reported. With sodium in HMPA containing *tert*-butanol,[306] non-hindered, secondary acetates give ~2:1 ratios of reduced to deacylated products. This method is very effective for tertiary acetates, where the increased stability of the radical favors C–O scission in the initially formed radical anion. Alkenes are reduced in this system.

Both primary and secondary alcohols are deoxygenated by reducing the derived, *N*,*N*-disubstituted thiocarbamates (Eq. 113).[307]



(Eq. 113)

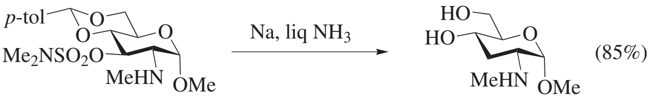
The best results are obtained by reducing the *N,N,N′,N′*-tetramethylphosphorodiamidates [ROP(O)(NMe$_2$)$_2$] of primary, secondary, or tertiary alcohols, using lithium in ethylamine containing 2–4 equivalents of *tert*-butanol with THF as the co-solvent.[308] The requisite derivatives are prepared in high yield from the lithium alkoxide and bis(dimethylamino)phosphoryl chloride.[308] For hindered substrates, using the corresponding dichloride followed by treatment with dimethylamine is recommended.[309] A typical example of the activation-reduction process is shown in Eq. 114.[308]



(Eq. 114)

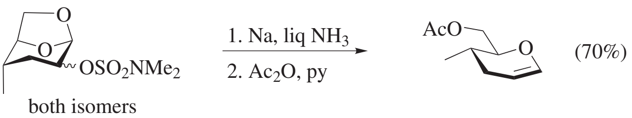
Reduction of aromatic rings is avoided by omitting the *tert*-butanol. By including ethanol in the reaction, concomitant deoxygenation and Birch reduction are possible.[308] Ketones and esters are reduced and must be protected, but isolated double bonds are not affected.

For some carbohydrate derivatives, reduction of *N,N*-dimethylsulfamates (ROSO$_2$NMe$_2$) with sodium in liquid ammonia is a viable process. In several examples of deoxygenation at C3 in pyranosides, hydroxyl groups in the 2- or 4-position do not suffer elimination. As expected, azides are reduced and *O*-benzylidene groups and *N*-(benzyloxycarbonyl) groups are removed under these conditions (Eq. 115).[310] Similar reductions of 3-*O*-triflates[300] and phosphoramidates[311] have been achieved. Arenesulfonates give only the parent alcohol.



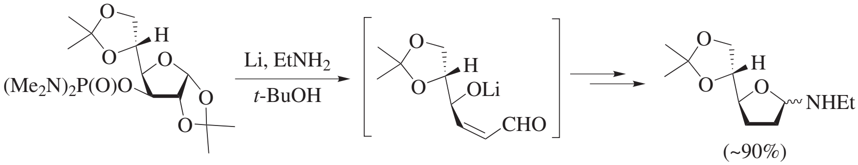
(Eq. 115)

Although these specific C3 reductions pose no problem, β-elimination from the intermediate carbanion is possible in dissolving-metal reductions of substrates whose structures allow for such elimination. The ring-opening of a 1,6-anhydrosugar with sodium in liquid ammonia illustrates this vulnerability (Eq. 116).[312]



(Eq. 116)

Furanoside derivatives undergo similar fragmentations. When an aldehyde equivalent is liberated, further reactions form an unstable glycosylamine, corresponding to a double deoxygenation (Scheme 13).[311]



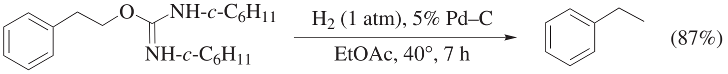
Scheme 13

Reductions of alkyl mesylates and triflates are also achieved using excess lithium sand in THF in the presence of a catalytic amount of 4,4′-di-*tert*-butylbiphenyl plus one or more equivalents of either nickel(II) chloride dihydrate[313] or the corresponding copper(II) salt.[314] Reductions of alkenes and arenes occur in the nickel-based system.

Allylic and benzylic alcohols form a special sub-group with respect to dissolving-metal reductions. Cleavage of the C−O bond is sufficiently facile that the alcohols, ethers, and acyl derivatives are deoxygenated by sodium or lithium in ammonia. These reductions are usually carried out in the presence of an additional proton source.[315]

Electrochemical Reductions. Primary and secondary mesylates are reduced, with yields in the 60−85% range, by electrolysis in DMF containing tetraethylammonium tosylate.[316] Slow addition of the substrate to the cathode compartment is necessary to minimize hydrolysis. Esters, nitriles, and isolated epoxides and double bonds are unaffected but β-oxy substituents are eliminated, indicating that reduction of the intermediate radical to a carbanion is taking place.

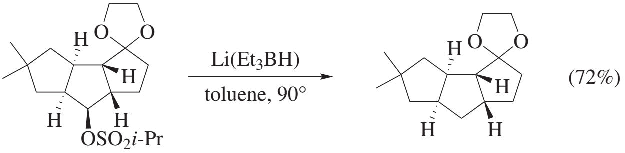
Hydrogenolysis of Alcohols and Their *O*-Derivatives. Saturated alcohols and their ethers, esters, and sulfonates are unaffected by catalytic hydrogenation. The copper(I) chloride-catalyzed reaction of an alcohol with dicyclohexylcarbodiimide (DCC) affords the corresponding *O*-alkyl urea, and these derivatives undergo hydrogenolysis over palladium. The method is suitable only for primary alcohols and acyclic secondary alcohols (Eq. 117). With cycloalkanols, the reductions proceed very slowly, and both eliminations and skeletal rearrangements can occur.[317]



(Eq. 117)

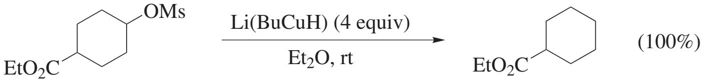
Direct hydrogenolysis of benzylic alcohols and their esters, ethers, or carbamates, usually with palladium catalysts, is achieved with molecular hydrogen or under transfer-hydrogenation conditions using ammonium formate or cyclohexene as the hydrogen source.[315,318] Allylic alcohols and their derivatives also undergo hydrogenolysis under these conditions, but competing saturation of the double bond in both starting material and product is a serious complication.[315]

Reductions Using Metal Hydrides. *Reductions of O-Sulfonates.* Hydride reductions of *O*-sulfonates with the reagents described below are often the method of choice for deoxygenating primary alcohols when other reducible groups, such as ketones, are absent or protected. Tosylates and mesylates of primary alcohols, and also of relatively unhindered secondary alcohols in predominantly hydrocarbon-like environments, are reduced by lithium aluminum hydride ($LiAlH_4$).[319] Superior results are obtained using lithium triethylborohydride ($LiEt_3BH$).[320,321] By using 2-propanesulfonates, competing O–S cleavage is minimized and more hindered substrates are reduced (Eq. 118).[322]



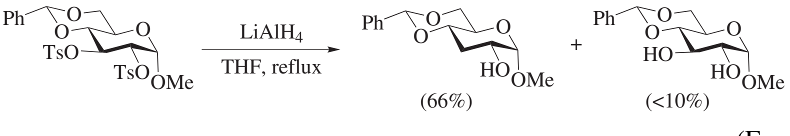
(Eq. 118)

Mesylates of primary alcohols can be reduced with sodium borohydride in DMSO[323] (secondary mesylates are unaffected[324]) and by sodium cyanoborohydride in HMPA, although the latter reactions are sluggish.[325] Complex copper(I) hydrides have also been used. A reagent formed by treating copper(I) iodide with two equivalents of lithium trimethoxyaluminum hydride reduces simple primary and acyclic secondary mesylates,[326] and the related reagent Li(BuCuH) reduces a cyclic, ester-containing substrate with complete selectivity (Eq. 119).[327] No examples of the application of these reagents to more highly functionalized systems are available.



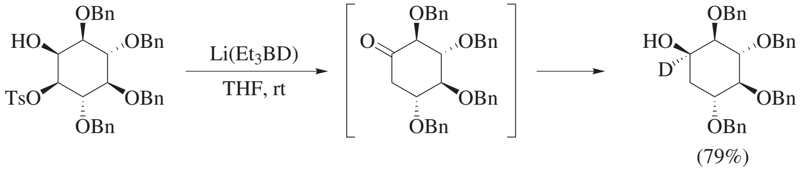
(Eq. 119)

In carbohydrates and similar, multi-heteroatom-substituted systems, the attack of a hydride reagent on the secondary carbon atom is inhibited by the polarizing and coordinating effects of nearby electron-withdrawing groups and by repulsion from lone pairs. With $LiAlH_4$, both ring-contracting rearrangements and O–S bond cleavage compete with deoxygenation in reductions of tosylates at the 2-, 3-, or 4-position in pyranosides.[328] In specific cases, deoxygenated products are obtained in good yield. Reduction by $LiAlH_4$ of a 2,3-ditosylate derived from D-glucose (Eq. 120) affords the 3-deoxy compound.[329] The formation of the 3-deoxy compound in this case may involve a direct displacement rather than the suggested intermediacy of the allo-configured 3,4-epoxy compound, since $LiAlH_4$ reduction of the latter substance gives predominantly the 2-deoxyallose derivative.[329a]



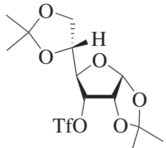
(Eq. 120)

From monotosylates of some *cis*-1,2-diols, net monodeoxygenation with LiEt$_3$BH is achieved via a hydride shift with loss of sulfonate, followed by reduction of the resulting ketone. An example in a cyclitol, where the use of a deuteriated reagent confirms the details of the process, is shown in Eq. 121.[330] A similar hydride shift process occurs in nucleoside derivatives.[331]

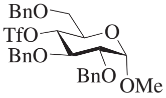


(Eq. 121)

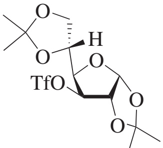
For substrates where rearrangements are not an issue, highly nucleofugal triflates afford a wider substrate scope because they are reduced by reagents that are both more functional-group sparing and less Lewis acidic.[332] Sodium borohydride in acetonitrile reduces some secondary triflates in protected carbohydrates, including the allofuranose **77** and the glucopyranose **78**, but the more hindered glucofuranose **79** gives mostly O–S cleavage and elimination products.[333]



77

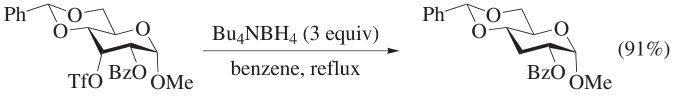


78



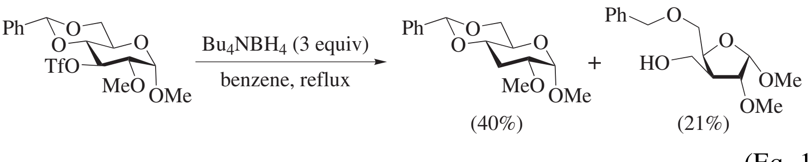
79

However, tetra-n-butylammonium borohydride (n-Bu$_4$NBH$_4$) in benzene or toluene at reflux reduces **79** to the 3-deoxy compound and also effects the deoxygenation of diverse pyranoside triflates, including the example shown in Eq. 122.[334]



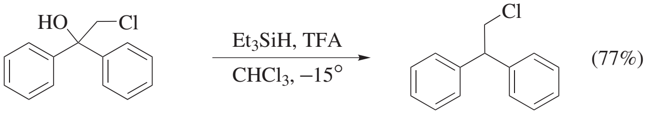
(Eq. 122)

A similar deoxygenation at C2 of a glucopyranoside triflate is achieved using Bu$_4$NBH$_4$ in benzene with ultrasonication,[335] but limitations are encountered in reductions of equatorial 3-triflates, where rearrangement accompanies reduction (Eq. 123).[334]



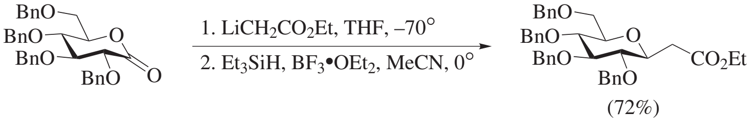
(Eq. 123)

Ionic Hydrogenations. Alcohols that can form a sufficiently stabilized carbenium ion are reduced by treatment with a Brønsted or Lewis acid in the presence of triethylsilane or a similar, relatively acid-stable hydride donor, a process usually referred to as ionic hydrogenation. A comprehensive review of silane-based reductions of this type is available.[336] The reduction of simple, secondary alcohols requires powerful promoters such as trifluoromethanesulfonic acid or tris(pentafluorophenyl)boron and is frequently accompanied by rearrangement and oligomerization processes. However, tertiary alcohols generally respond favorably provided that there are no nearby electron-withdrawing groups. Ionic hydrogenation is very effective for reducing benzylic alcohols. In contrast to radical-based and most other methods, halogens are unaffected even when they are β to the center undergoing reduction (Eq. 124).[337]



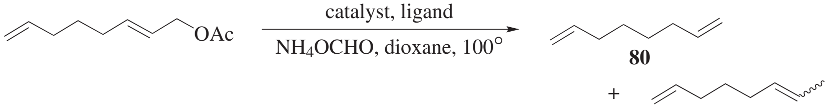
(Eq. 124)

Local effects from electron-withdrawing groups must be offset by strong resonance stabilization of the carbenium ion for reduction to succeed. The stereocontrolled preparation of *C*-glycosides, via reduction of the anomeric oxocarbenium ion,[338,339] is such a case (Eq. 125).[338]



(Eq. 125)

Reductions Involving Metal Complexes. Allylic ethers, esters, carbonates, or carbamates are reduced, via an intermediate π-allyl complex, with a catalytic amount of a palladium(0) complex in the presence of a hydride source.[315,340] The most frequently used combination is formate as the *H*-donor plus catalytic tetrakis(triphenylphosphine)palladium(0). However, significant control over the site selectivity of reduction can be exerted by varying the hydride source, the leaving group, and the ligands on the catalyst (Eq. 126).[340] The ratio of isomers **80** and **81** shifts markedly when the ligand/palladium source is changed from $PPh_3/Pd(OAc)_2$ to $PBu_3/Pd_2(dba)_3$.



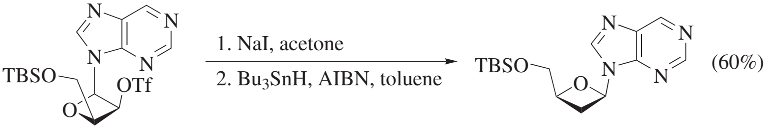
80

81

Catalyst	Ligand	Yield (%) **80** + **81** (GC)	**80**:**81**
$Pd(OAc)_2$	PPh_3	100	68:32
$Pd_2(dba)_3•CHCl_3$	PBu_3	100	100:0

(Eq. 126)

Formation and Reduction of Other C−X Bonds. Overall deoxygenation of an alcohol is achieved by converting the C−O bond into a C−Cl, C−Br, C−I, or C−S bond, followed by reduction of the halo compound with zinc-acetic acid or Bu_3SnH, or by catalytic hydrogenation. Raney nickel is used for desulfurizations. Most frequently, the displacement of a sulfonate by iodide ion is the first step. An example in the oxetanocin system is shown in Eq. 127.[341]

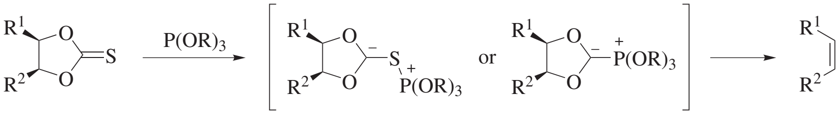


(Eq. 127)

This process is limited by competing rearrangements in the displacement step, especially in hindered, heteroatom-substituted systems,[332] but is usually very effective for primary alcohols. When β-oxygen substituents are present, Bu_3SnH or hydrogenation must be used for the reduction step to avoid eliminations. One-pot activation-reduction of benzylic alcohols is achieved by heating with diphosphorus tetraiodide in benzene.[342]

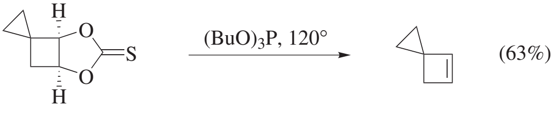
Alkene Formation from Diols

Methods for converting 1,2-diols into alkenes have been comprehensively reviewed.[343] When cyclic thiocarbonates are heated with trialkyl phosphites (the Corey-Winter reaction[344,345]), efficient alkene formation occurs (Scheme 14). Although the nature of the immediate precursor to the alkene is not known with certainty, the dioxolane-derived carbene is not involved.[344] The process is concerted and stereospecific and shows no evidence of the development of either ionic or radical character at the reacting carbon centers.



Scheme 14

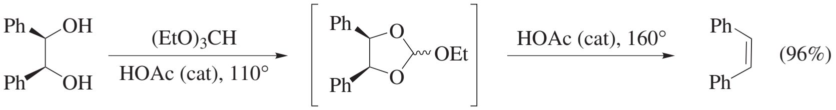
This method allows the synthesis of alkenes not accessible by other methods, including the spirocyclic example shown in Eq. 128[346] and also the generation and trapping of highly strained products such as (*E*)-cycloheptene.[345] Olefin formation at lower temperatures is achieved by replacing the phosphite with a 1,3,2-diazaphospholidine.[83]



(Eq. 128)

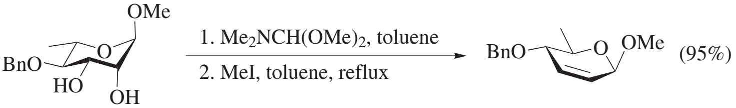
The method has wide applicability, and side-reactions are infrequent. When trimethyl phosphite is used, *N*-methylation of nucleosides by the thionophosphate co-product can occur.[347] Cyclic thiocarbonates are also converted into alkenes by bis(1,5-cyclooctadiene)nickel(0)[348] and by iron pentacarbonyl.[349] Isomerization of strained alkenes occurs with these reagents. Direct, but nonstereospecific, reductions of diols take place by reaction with titanium(III) chloride and potassium[350] and by treating the bis(alkoxides) with potassium hexachlorotungstate(IV).[351]

Diols are converted stereospecifically into alkenes on heating with trialkyl orthoformates and a catalytic amount of a carboxylic acid (Eq. 129).[352]



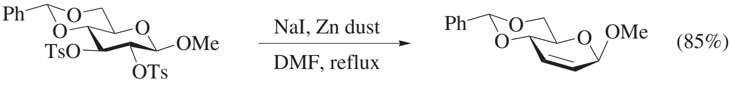
(Eq. 129)

Although elevated temperatures are needed, the near-neutral conditions accommodate a wide range of substrates. Related methods involve converting the diol into the corresponding 2-dimethylamino-1,3-dioxolane, followed by treatment with either acetic anhydride[353] or iodomethane (Eq. 130).[354]



(Eq. 130)

For molecules that are otherwise stable to alkyllithium compounds, deprotonation (with *n*-BuLi) of 2-phenyl-1,3-dioxolanes results in the concerted loss of benzoate anion to give the alkene.[343] For more sensitive molecules, displacement-reductive elimination sequences can be employed. Reaction of a bis(*O*-mesyl) derivative with sodium iodide and zinc dust is effective.[355] This method enables the conversion of *trans*-diols contained in 4- to 7-membered rings into the *cis*-alkenes. This method is not dependent on the relative configuration of the diol, but does require that one of the mesylates be capable of experiencing S_N2 displacement by iodide ion to set up the subsequent reductive elimination. This reaction is frequently used in carbohydrate chemistry (Eq. 131)[356] and provides an ionic alternative to the bis(xanthate) route.



(Eq. 131)

Reactions of cyclic thiocarbonates with iodomethane[82] or 2-iodopropane[357] also produce substrates for reductive elimination. Dissolving-metal conditions can be used to obtain alkenes from bis(*O*-mesyl) derivatives[358] and from cyclic phosphates or phosphoramidates.[359,360]

EXPERIMENTAL CONDITIONS

Reaction Conditions

Reductions using Bu_3SnH and other nonionic reducing agents are typically conducted in an atmosphere of nitrogen or argon in aromatic hydrocarbon solvents at temperatures of 80–120°. Higher temperatures may be appropriate for primary alcohol derivatives and lower temperatures can be used for secondary and tertiary substrates when appropriate initiation is provided. Radical reactions are very solvent-tolerant; deoxygenations may also be carried out in dioxane, alkanes, acetone, ethyl acetate, acetonitrile, and even dichloromethane. Dimethylformamide is used for the persulfate–formate system, and alcohol solvents are suitable for reductions using hypophosphites; the inclusion of phase-transfer agents permits water to be used. Initiators (usually azo compounds such as AIBN, peroxides such as Bz_2O_2, or the trialkylborane–air combination) are advisable in all cases and are essential when H-donors that are less efficient than Bu_3SnH are used. For relatively weak H-donors, the gradual addition of 0.5–2 equivalents of initiator may be needed to offset chain-termination events.

Isolation of Products

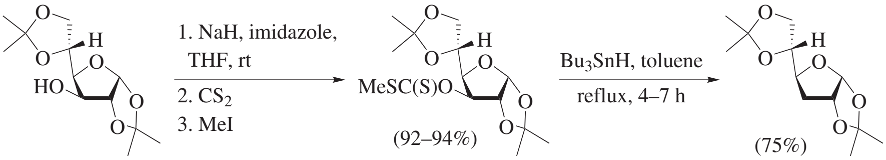
As noted earlier, although a variety of alternative systems are available, the majority of reported, lab-scale deoxygenations use Bu_3SnH. This substance and hydrolytically stable co-products such as Bu_3SnSMe can pose separation problems when the reduction product is very non-polar, and their conversion into the organotin halide (Bu_3SnHal) is advisable. For Bu_3SnH, this is achieved by heating with CCl_4 or CCl_3Br. Iodine converts both Bu_3SnH and Bu_3SnSMe into Bu_3SnI. When these halides, and also reduction co-products such as Bu_3SnIm and Bu_3SnOAr, are subjected to aqueous work-up and/or chromatography, gradual hydrolysis to $(Bu_3Sn)_2O$ takes place. Complete hydrolysis of the halides is achieved by pretreatment with DBU in wet ether,[361] but the subsequent streaking of $(Bu_3Sn)_2O$ on column or plate chromatography can lead to the contamination of moderately polar reduction products. Three solutions to this problem are available. The first is to partition the residue (after evaporating the reaction solvent) between acetonitrile and hexane to extract tin compounds into the hydrocarbon phase.[362] This method is not appropriate when the reduction product is very non-polar. A second alternative is to treat an ethereal solution of the crude reaction product, after conversion of any excess Bu_3SnH into Bu_3SnHal by iodine or carbon tetrachloride, with aqueous potassium fluoride solution.[59,363] This process precipitates insoluble, polymeric tri-*n*-butyltin fluoride, which is removed by filtration. A third approach, when the product is moderately to very polar, involves treating the crude reaction products with $NaBH_3CN$ in *tert*-butanol, followed by work-up and chromatography.[105] This process allows regeneration and recovery of Bu_3SnH from xanthate reductions.

The higher volatility of low-molecular weight silanes avoids some of these problems, although the fate of co-products derived from these reagents has not been examined. The best choice, with respect to minimizing both work-up and toxicity issues, would presumably employ low-molecular weight P–H based reducing agents, notably H_3PO_2 and its salts. The need to use large amounts of initiator in reductions with most P–H and Si–H based reagents, and the tendency of the former to add to olefins, can offset these advantages.

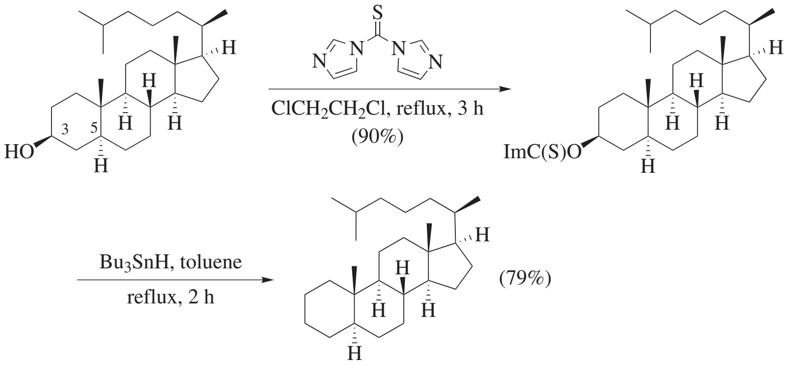
Hazards

Although inorganic tin compounds are relatively harmless, both alkyl- and aryltin compounds exhibit significant mammalian toxicity.[364,365] *Microorganisms, notably protozoa and fungi, are sensitive to submicromolar concentrations of some dialkyl- and trialkyltin compounds,*[364] *so care should be taken to ensure that deoxygenation products for biological evaluations are completely free of organotin impurities.* Bu_3SnH *is appreciably volatile (bp 80° at 1 mm Hg). All reactions involving this reagent should be conducted in a ventilated hood, and precautions should be taken to avoid skin contact. In addition, reductions of ROC(S)Y species when Y is a heteroatom generate COS, which is malodorous and toxic. Entraining in nitrogen and passing the resulting gases through a mixed NaOH–NaOCl solution will trap COS. In most xanthate preparations,* CS_2 *is required. This substance is both highly volatile and toxic. It has a very low flash point, so contact of the liquid or vapor with hot surfaces must be avoided.*

EXPERIMENTAL PROCEDURES

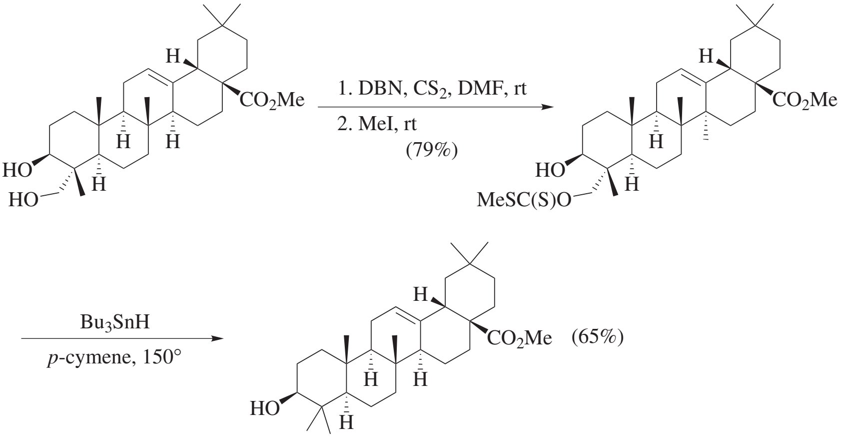


3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose [Deoxygenation of a Secondary *O*-(Methylthiothiocarbonyl) Derivative with Bu_3SnH]. This procedure is found in *Organic Syntheses*.[56]



5α-Cholestane [Deoxygenation of a Secondary *O*-(Imidazol-1-ylthiocarbonyl) Derivative with Bu_3SnH].[1] 5α-Cholestan-3β-ol (2.50 g, 6.44 mmol) and 1,1′-thiocarbonyldiimidazole (2.00 g, 11.22 mmol) were heated under reflux for 3 h in 1,2-dichloroethane (25 mL). The solvent was evaporated, the residue was dissolved in CH_2Cl_2, and the solution was washed with 5% w/v tartaric acid, H_2O, and saturated $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated. The residue was recrystallized from Et_2O/MeOH, by evaporating the Et_2O at rt on a rotary evaporator, to give 1-(5α-cholestan-3β-yloxythiocarbonyl)imidazole (2.92 g, 90%): mp 151–152°; $[\alpha]_D^{22}$ −57.2 (*c* 0.8, $CHCl_3$); IR (Nujol) 1410, 1305, 1265, 1125, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.33 (s, 1H), 7.62 (s, 1H), 7.02 (s, 1H), 5.42 (m, 1H). Anal. Calcd for $C_{31}H_{50}N_2OS$: C 74.65; H, 10.1; N, 5.6; S, 6.4. Found: C, 74.6; H, 9.9; N, 5.65; S, 6.4.

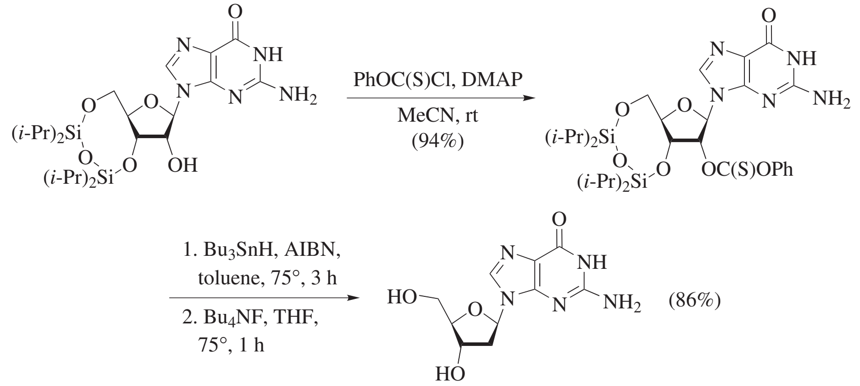
A solution of the foregoing compound (0.51 g, 1.022 mmol) in toluene (25 mL) was added over 0.5 h to a refluxing solution of Bu_3SnH (0.45 g, 1.55 mmol) in toluene (20 mL) under argon. The solution was heated at reflux until TLC indicated complete consumption of the starting material (1.5 h). The solution was evaporated and the residue chromatographed on alumina (Brockmann grade III), eluting with pentane. Evaporation of the product-containing fractions and recrystallization from acetone/methanol gave 5α-cholestane (0.30 g, 79%); mp and mixed mp with an authentic sample, 78.5–79.5°.



Methyl Oleanolate [Deoxygenation of a Primary *O*-(Methylthiothiocarbonyl) Derivative with Bu_3SnH Using the Potassium Fluoride Work-Up Procedure].[59] Hederagenin methyl ester (0.10 g, 0.21 mmol) was stirred at rt in DMF (1 mL) and DBN (0.10 g, 0.81 mmol) was added, followed by CS_2 (1 mL). After 30 min, MeI (1 mL) was added and stirring was continued for 30 min. The solution was then evaporated under high vacuum and the residue was dissolved in EtOAc (5 mL) and washed with H_2O (5 mL) and brine (2 mL), dried ($MgSO_4$), and evaporated. The crude product was filtered through a small column of silica (EtOAc/hexanes 3:2). Pure fractions were concentrated and the residue was recrystallized from EtOH/H_2O to give the mono-xanthate (0.094 g, 79%): mp 173–175°; $[\alpha]_D^{16}$ + 16 (*c* 1, $CHCl_3$); IR ($CHCl_3$)1720, 1150, 1060 cm^{-1}; ^1H

NMR (100 MHz, $CDCl_3$) δ 5.2 (m, 1H), 4.47 (q, 2H), 3.54 (s, 3H), 2.53 (s, 3H). Anal. Calcd for $C_{33}H_{52}O_4S_2$: C, 68.7; H, 9.1; S, 11.1. Found: C, 68.6; H, 9.15; S, 11.0.

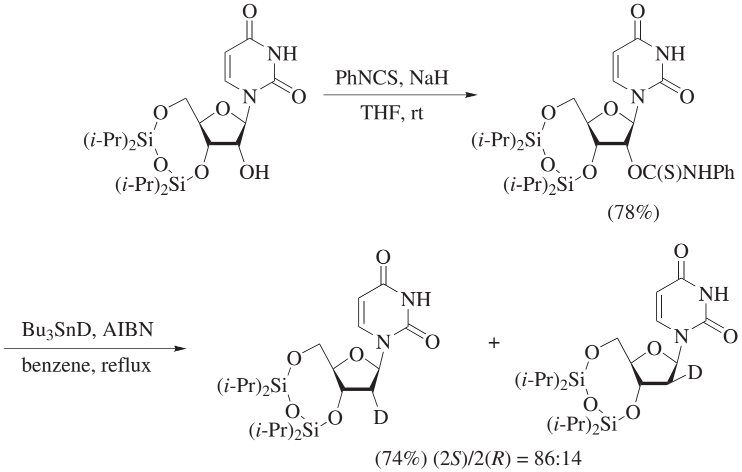
A solution of the foregoing compound (0.05 g, 0.087 mmol) in *p*-cymene (3 mL) was heated under argon at 150°, and a solution of Bu_3SnH (0.20 g, 0.69 mmol) in *p*-cymene (3 mL) was added over 2 h. The solution was then heated at reflux for 10 h. The solvent was evaporated and the residue was heated at reflux for 3 h in CCl_4 (20 mL). The solution was evaporated and the residue was treated with a solution of iodine in Et_2O until a permanent iodine color remained. After dilution with Et_2O, the solution was shaken with KF in H_2O (5% w/v, 10 mL). The solid (Bu_3SnF) was removed by filtration and washed with Et_2O, and the organic phase was dried ($MgSO_4$) and evaporated. A solution of the crude product was filtered through a short column of silica (hexanes/EtOAc 4:1). Pure fractions were pooled and evaporated to give methyl oleanolate (0.026 g, 65%), identical with an authentic sample.



2′-Deoxyguanosine [Deoxygenation of a Secondary *O*-(Phenoxythiocarbonyl) Derivative with Bu_3SnH].[34] A solution of 3′,5′-*O*-(1,1,3,3-tetraisopropyldisilox-1,3-diyl)guanosine (1.05 g, 2.00 mmol) in anhydrous MeCN (30 mL) was treated with DMAP (0.50 g, 4.10 mmol) and phenoxythiocarbonyl chloride (0.40 mL, 2.2 mmol), and stirred overnight at rt. The solvent was evaporated and the residue was partitioned in EtOAc/H_2O. The organic phase was washed successively with 1 M HCl, H_2O, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and evaporated. The residue was recrystallized from EtOH/H_2O (95:5) to give 2′-*O*-phenoxythiocarbonyl-3′,5′-*O*-(1,1,3,3-tetraisopropyldisilox-1,3-diyl)guanosine (1.25 g, 94%): mp 255–258°; UV (EtOH) max 250 nm (ε 16,700); HRMS: M^+ calcd for $C_{29}H_{43}N_5O_7SSi_2$, 661.2414; found, 661.2436.

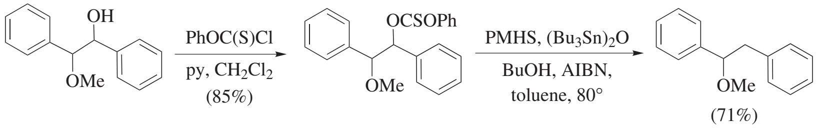
A solution of the foregoing compound (1.00 g, 1.51 mmol), Bu_3SnH (0.60 mL, 2.25 mmol), and AIBN (0.05 g, 0.30 mmol) in toluene (30 mL) was degassed with oxygen-free N_2 and heated at 75° for 3 h under N_2. Tetra-*n*-butylammonium fluoride (1 M in THF; 3.0 mL) was added, and heating at 75° was continued for 1 h. The solvent was evaporated and the residue was partitioned between Et_2O and

H_2O. The aqueous phase was concentrated and applied to a column of Dowex 1-X2 (OH^-) ion-exchange resin. The column was washed well with H_2O and the product was eluted with triethylammonium bicarbonate buffer (0.25 M in H_2O, pH 9.0). The eluate was evaporated and the residue was treated with H_2O (15 mL) and evaporated. Addition and evaporation of H_2O was repeated four times, and the final residue was recrystallized from H_2O to afford 2′-deoxyguanosine (0.347 g, 86%), mp 251–252°, identical with an authentic sample.



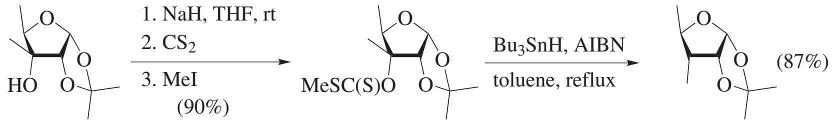
(2′*S* and 2′*R*)-2-Deuterio-3′,5′-*O*-(1,1,3,3-tetraisopropyldisilox-1,3-diyl)-2′-deoxyuridine [Deoxygenation of a Secondary *O*-(*N*-Phenylthiocarbamoyl) Derivative with Bu_3SnD].[39] A mixture of 3′,5′-*O*-(1,1,3,3-tetraisopropyldisilox-1,3-diyl)uridine (4.87 g, 10.0 mmol), phenyl isothiocyanate (1.49 g, 11.0 mmol), and THF (20 mL) was stirred at rt, and NaH (60% in oil; 0.44 g, 11.0 mmol) was added. Stirring was continued overnight. The solvent was evaporated and the residue was diluted with H_2O (50 mL), extracted with CH_2Cl_2 (50 mL), and the organic phase was dried ($MgSO_4$) and evaporated. The crude product was chromatographed on silica, eluting with a gradient of EtOAc in hexanes, and the pure fractions were pooled and evaporated to afford 2-*O*-(*N*-phenylthiocarbamoyl)-3′,5′-*O*-(1,1,3,3-tetraisopropyldisilox-1,3-diyl)uridine (4.85 g, 78%) as an amorphous solid: IR (KBr) 3240, 2946, 2868, 1692, 1600, 1543, 1499, 1464, 1271, 1221, 1181, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55–7.15 (m, 6H), 6.15 (d, $J = 4.9$ Hz, 1H), 8.76 (br, 1H), 8.67 (br, 1H), 5.71 (br, 2H), 4.72 (br, 1H), 4.15 and 4.02 (AB, $J = 13.0$ Hz, 2H), 3.90 (br, 1H), 1.14–1.00 (m, 28H); ^{13}C NMR ($CDCl_3$) δ 187.2, 162.6, 149.5, 140.7, 137.1, 129.1, 125.9, 122.5, 102.5, 90.4, 82.6, 81.6, 68.9, 60.5, 17.4, 17.3, 17.2, 17.2, 17.1, 17.0, 17.0, 16.8, 13.4, 13.0, 12.9, 12.7; EI-HRM: $[M - PhNCS - C_3H_7 + H]^+$ calcd for $C_{18}H_{31}O_7N_2Si_2$, 443.1670; found, 443.1670.

A mixture of the foregoing compound (0.124 g, 0.20 mmol), Bu_3SnD (0.117 g, 0.40 mmol), and AIBN (0.066 g, 0.04 mmol) in benzene (4 mL) was heated at reflux under argon for 4 h. The solvent was evaporated and the residue chromatographed on silica (hexanes/EtOAc, 7:3) to afford ($2'S + 2'R$)-2-deuterio-3′,5′-*O*-(1,1,3,3-tetraisopropyldisilox-1,3-diyl)uridine as a viscous oil (0.070 g, 74%). The deuterium content (100%) and the (2*S*)/(2*R*) ratio (86:14) were determined by ^{1}H NMR. ^{1}H NMR ($CDCl_3$) δ 8.68 (br, 1H), 7.78 (d, $J = 8.1$ Hz, 1H), 5.69 (d, $J = 8.1$ Hz, 1H), 4.13 (dd, $J = 8.4$, 7.0 Hz, 1H), 4.01 (dd, $J = 13.2$, 2.9 Hz, 1H), 2.49 (dd, $J = 10.5$, 7.0 Hz, 0.14H), 2.24 (d, $J = 6.9$ Hz, 0.86H), 1.11–0.90 (m, 28H); ^{13}C NMR ($CDCl_3$) δ 162.8, 149.9, 139.6, 101.8, 85.3, 84.4, 67.7, 60.5, 39.8 (*t*, $J = 20.1$ Hz), 17.5, 17.4, 17.3, 17.3, 17.1, 17.0, 16.9, 16.8, 13.5; EI-HRMS: $[M + H]^+$ calcd for $C_{21}H_{38}O_6N_2Si_2D$, 472.2409; found, 472.2381.



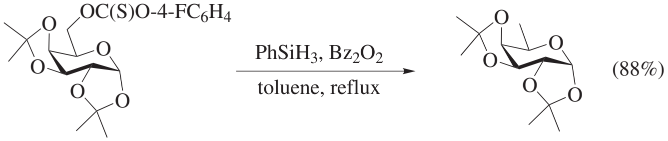
1,2-Diphenyl-1-methoxyethane [Deoxygenation of a Secondary *O*-(Phenoxythiocarbonyl) Derivative with Poly(methylhydrosiloxane) and Catalytic $(Bu_3Sn)_2O$].[92] 2-Methoxy 1,2-diphenylethanol (3.00 g, 13.0 mmol, 3:1 mixture of diastereomers) in toluene (50 mL) was evaporated, and the dried alcohol was stirred at 0° in CH_2Cl_2 (50 mL) and treated with pyridine (1.23 g, 15.6 mmol) and phenoxythiocarbonyl chloride (2.47 g, 14.3 mmol). The mixture was stirred at rt for 1.5 h, diluted with CH_2Cl_2 (50 mL), washed with 2 N HCl (2 × 75 mL) and H_2O (2 × 75 mL), dried ($MgSO_4$), and evaporated. Flash chromatography (silica gel, hexanes/EtOAc, 20:1) afforded 1,2-diphenyl-1-methoxy-2-(phenoxythiocarbonyloxy)ethane (4.50 g, 85%) as a colorless oil: IR (neat) 1492, 1274, 1198, 1116, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): both isomers δ 7.60–6.92 (m, 15H); major isomer δ 6.39 (d, $J = 5.5$ Hz, 1H), 4.69 (d, $J = 5.5$, 1H), 3.28 (s, 3H); minor isomer δ 6.37 (d, $J = 7.5$ Hz, 1H), 4.62 (d, $J = 7.5$ Hz, 1H), 3.34 (s, 3H); ^{13}C NMR ($CDCl_3$): major isomer δ 193.8, 153.4, 137.0, 135.4, 129.5, 128.5, 128.3, 128.1, 128.0, 126.5, 121.9, 87.5, 85.0, 57.4; minor isomer δ 194.2, 153.5, 136.8, 135.6, 122.0, 88.2, 85.8, 57.3 (other resonances of the minor isomer were obscured). Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.5; H, 5.5. Found: C, 72.55, H, 5.7.

Poly(methylhydrosiloxane) (0.30 g, 5.00 mmol), 1-butanol (0.50 mL, 5.46 mmol), AIBN (0.025 g, 0.15 mmol), and bis(tri-*n*-butyltin) oxide (0.019 mL, 0.037 mmol) were added to a solution of the foregoing thiocarbonate (0.365 g, 1.00 mmol) in toluene (1 mL). The mixture was stirred under argon at 80° for 8 h. Additional AIBN (0.025 g, 0.15 mmol) and bis(tri-*n*-butyltin) oxide (0.019 mL, 0.037 mmol) were added and heating and stirring were continued for 16 h. After the mixture had cooled to rt, it was diluted with THF (10 mL), stirred, and then 2 N NaOH (10 mL) was added slowly (*caution*: H_2 evolution!). The mixture was loosely capped and stirred for 3 h, and the product was extracted with Et_2O (2 × 15 mL). The combined organic phases were washed with 1 N HCl (2 × 10 mL) and brine (15 mL), and dried over $MgSO_4$. After evaporation, the crude product was purified by flash chromatography (silica gel, hexanes/EtOAc, 99:1) to give 1,2-diphenyl-1-methoxyethane (0.165 g, 71%) as a colorless oil. IR (neat) 2922, 2851, 1603, 1454, 1101, 1072, 1029, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35–7.12 (m, 10H), 4.36 (dd, $J = 7.6$, 5.8 Hz, 1H), 3.22 (s, 3H), 2.92 (dd, $J = 7.6$, 5.8 Hz, 1H); ^{13}C NMR ($CDCl_z$) δ 141.8, 131.7, 129.7, 128.5, 128.3, 127.8, 127.0, 126.3, 85.3, 57.0, 45.0; EI-HRMS: M$^+$ calcd for $C_{15}H_{16}O$, 212.1201; found, 212.1202.

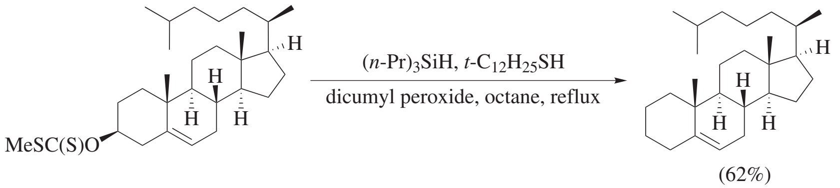


3,5-Dideoxy-1,2-*O*-isopropylidene-3-methyl-α-D-*ribo*-pentofuranose [Deoxygenation of a Tertiary *O*-(Methylthiothiocarbonyl) Derivative with Bu_3SnH].[40] A solution of 3,5-dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-ribofuranose (1.17 g, 6.22 mmol) in THF (13 mL) was added to a stirred suspension of NaH (60% in oil, 0.62 g, 15.5 mmol, previously washed with hexanes) under N_2. Hydrogen evolved. After 0.5 h, CS_2 (2.0 mL, 33.3 mmol) was added and after a further 1 h, MeI (1.0 mL, 16.0 mmol) was added. The reaction was quenched with several drops of methanol and the solution was diluted with H_2O. The product was extracted with CH_2Cl_2. The organic phase was washed with 10% $NaHSO_4$, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and evaporated. Column chromatography (silica gel, gradient from 0:1 to 1:3 EtOAc/hexanes) gave 3,5-dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-3-*O*-(methylthiothiocarbonyl)-α-D-*ribo*-pentofuranose (1.55 g, 90%): mp 93–94° (hexanes); $[\alpha]_D^{23}+142$ (*c* 0.59, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.16 (d, $J = 4$ Hz, 1H), 4.30 (q, 1H), 2.52 (s, 3H), 1.58 (s, 3H), 1.54 (s, 3H), 1.32 (s, 3H), 1.27 (d, $J = 6.4$ Hz, 3H); FAB-MS (m/z): $[M + H]^+$ 279. Anal. Calcd for $C_{11}H_{18}O_4S_2$: C, 47.5; H, 6.5; S, 23.0. Found: C, 47.5, H, 6.4; S, 22.5.

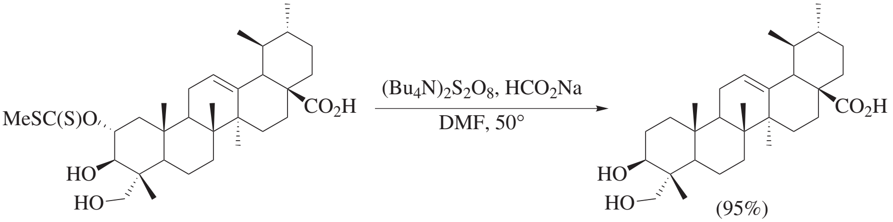
A solution of the foregoing xanthate (1.05 g, 3.78 mmol), Bu_3SnH (1.52 mL, 4.83 mmol), and AIBN (0.030 g, 0.18 mmol) in toluene (25 mL) was heated at reflux under N_2 for 2.5 h. The solution was evaporated and the residue was chromatographed (silica gel, gradient from 0:1 to 1:50 acetone/hexanes) to afford 3,5-dideoxy-1,2-*O*-isopropylidene-3-methyl-α-D-*ribo*-pentofuranose (0.536 g, 87%) as a colorless liquid: $[\alpha]_D^{23}+32.9$ (*c* 0.78, $CHCl_3$); lit.[366] $[\alpha]_D^{23}+36.1$ (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.78 (d, $J = 3.5$ Hz, 1H), 4.53 (dd, $J = 3.5$, 3.5 Hz, 1H), 3.82 (dq, $J = 6.5$, 10 Hz, 1H), 1.59 (s, 3H), 1.56 (m, 1H), 1.31 (s, 3H), 1.22 (d, $J = 6.0$ Hz, 3H), 1.03 (d, $J = 6.5$ Hz, 3H).



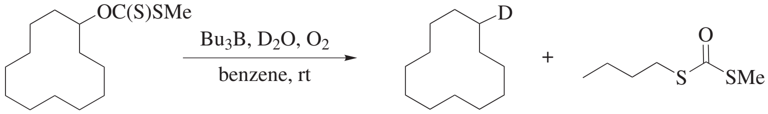
1,2:3,4-Di-*O*-isopropylidene-α-D-fucopyranose [Deoxygenation of a Primary *O*-(4-Fluorophenoxythiocarbonyl) Derivative with $PhSiH_3$].[367] Phenylsilane (0.10 mL, 0.80 mmol) was added to a solution of 1,2,3,4-di-*O*-isopropylidene-6-*O*-(4-fluorophenoxythiocarbonyl)-α-D-galactopyranose (0. 16 g, 0.40 mmol) in toluene (3 mL), and the solution was stirred and heated to reflux under argon. Successive portions (each 0.15 mL) of a solution of benzoyl peroxide (0.387 g) in toluene (3 mL) were added, with refluxing for 20 min following each addition. When TLC indicated the complete consumption of starting material, the solvent was evaporated and the residue was chromatographed (silica gel, hexane/EtOAc, 4:1) to afford 1,2:3,4-di-*O*-isopropylidene-α-D-fucopyranose (0.086 g, 88%) as a colorless liquid: $[\alpha]_D{}^{27}$ −60.0 (*c* 2, $CHCl_3$); IR ($CDCl_3$) 2988, 1379, 1101 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53 (d, $J = 6$ Hz, 1H), 4.60 (dd, $J = 2$, 8 Hz, 1H), 4.30 (dd, $J = 2$, 6 Hz, 1H), 4.09 (dd, $J = 2$, 8 Hz, 1H), 3.93 (dt, $J = 2$, 6 Hz, 1H), 1.53 (s, 3H), 1.47 (s, 3H), 1.33 (s, 3H),1.26 (d, $J = 6$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 108.8, 108.2, 96.5, 73.4, 70.9, 70.3, 63.4, 26.0 (2 C), 24.8, 24.3, 15.8; MS (*m/z*): 229 [M − 15], 113, 100, 83, 59, 43.



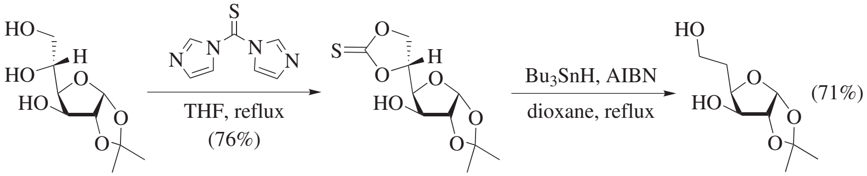
Cholest-5-ene [Deoxygenation of a Secondary *O*-(Methylthiothiocarbonyl) Derivative with Tri-*n*-propylsilane and a Catalytic Thiol].[170] A mixture of tri-*n*-propylsilane (1.33 g, 8.39 mmol), dicumyl peroxide (0.0136 g, 0.05 mmol), *tert*-dodecanethiol (0.005 g, 0.025 mmol), and 3β-(methylthiothiocarbonyloxy) cholest-5-ene (0.500 g, 1.04 mmol) in *n*-octane (3.5 mL) was heated and stirred at reflux under argon. After 2 h and 5 h, additions of *tert*-dodecanethiol (0.005 g, 0.025 mmol) in *n*-octane (0.5 mL) were made, and refluxing was continued for a further 3 h. The mixture was cooled and evaporated at 40° under high vacuum, and the residue was chromatographed (silica gel, hexane) to afford cholest-5-ene (0.24 g, 62%), mp 91–92.5°, identical with an authentic sample.



2-Deoxyasiatic Acid [Deoxygenation of a Secondary *O*-(Methylthiothiocarbonyl) Derivative with Tetrabutylammonium Persulfate and Sodium Formate].[211] A mixture of 2-*O*-(methylthiothiocarbonyl) asiatic acid (5.79 g, 10 mmol), sodium formate (4.08 g, 60 mmol), tetra-*n*-butylammonium persulfate (20.31 g, 30 mmol), and DMF (150 mL) was stirred and heated at 50° for 2 h. The mixture was poured into H_2O (400 mL) and extracted with CH_2Cl_2 (400 mL), and the organic phase was washed with H_2O (400 mL), dried (Na_2SO_4), and evaporated. The residue was recrystallized from methanol to afford 2-deoxyasiatic acid (4.49 g, 95%): mp 272–274°; R_f 0.21 (silica, EtOAc/hexane/EtOH, 1:2:0.1); $[\alpha]_D^{20} + 84.5$ (*c* 1, DMF); IR (KBr) 3414, 2926, 1695, 1454, 1389, 1233, 1191, 1045, 662 cm^{-1}; ^1H NMR (DMSO-d_6) δ 14.5–13.2 (br s, 1H), 5.13 (m, 1H), 3.45 (dd, $J = 10.8$, 5.1 Hz, 1H), 2.82 (d, $J = 10.8$ Hz, 1H), 2.59, (d, $J = 10.2$ Hz, 1H), 1.50 (d, $J = 10.8$ Hz, 1H), 1.45–1.16 (m, 4H), 1.02–0.85 (m, 7H), 0.82–0.57 (m, 5H), 0.46–0.42 (m, 4H), 0.36–0.16 (m, 8H), 0.19–0.14 (m, 6H); ^{13}C NMR (DMSO-d_6) δ 178.5, 138.5, 124.9, 70.6, 64.8, 52.6, 47.3, 47.1, 46.7, 42.1, 41.9, 39.3, 38.7 (2 C), 38.3, 36.6, 36.5, 30.4, 27.8, 26.8, 24.1, 23.1, 21.3, 17.7, 17.3, 17.2, 15.8, 12.9.

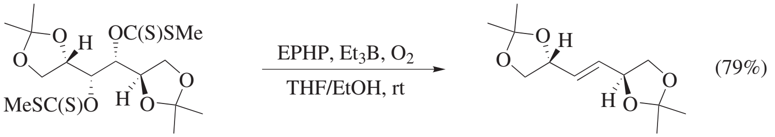


Deuteriocyclododecane [Deoxygenation of a Secondary *O*-(Methylthiothiocarbonyl) Derivative with a Trialkylborane, D_2O, and O_2, with Co-Product Isolation].[38] A solution of (methylthiothiocarbonyloxy)cyclododecane (0.145 g, 0.53 mmol) in dry benzene (17 mL) and D_2O (0.052 mL, 2.6 mmol) was stirred for 1 h at rt with a slow stream of argon passing through the solution. Tri-*n*-butylborane (*caution:* can ignite in air) (0.65 mL, 2.65 mmol) in benzene (0.35 mL) was added by syringe. Dry air (52 mL, 0.42 mmol of O_2) was introduced using a syringe pump at a rate of 1.2 mL/h through a stainless steel cannula positioned below the reaction surface. Hydrogen peroxide (30% in H_2O, 3 mL) and NaOH (3 M in H_2O, 3 mL) were then added simultaneously (*caution*: exothermic) and stirring was continued for 10 min. The solution was diluted with EtOAc (10 mL) and H_2O (10 mL), the organic phase was separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined extracts were dried (Na_2SO_4) and evaporated. Column chromatography (silica gel, EtOAc/hexanes, gradient 0:1 to 1:4) afforded deuteriocyclododecane (0.074 g, 83%, deuterium content 92%): mp 49–51° (hexanes); ^{1}H NMR ($CDCl_3$) δ 1.34 (s); ^{2}H NMR ($CHCl_3$) δ 1.33; EI-LRMS (m/z): 169.1. The later fractions from the chromatography afforded *S*-methyl-*S*-(*n*-butyl)dithiocarbonate as a pale yellow oil (0.084 g, 97%): IR (film) 2957, 2931, 1740, 1648, 1465, 867 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.99 (t, $J = 7$ Hz, 2H), 2.41 (s, 3H), 1.62–1.56 (m, 2H), 1.42–1.34 (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 190.0, 31.8, 30.4, 21.8, 13.5, 13.0.



1,2-*O*-Isopropylidene-5-deoxy-α-D-*ribo*-hexofuranose [Deoxygenation of a Cyclic Thiocarbonate with Bu_3SnH].[231] 1,2-*O*-Isopropylidene-α-D-*ribo*-hexofuranose (56 g, 255 mmol) was dissolved by heating in dry THF (2 L). The solution was cooled, 1,1′-thiocarbonyldiimidazole (50 g, 281 mmol) was added, and the solution was heated at reflux under N_2 for 2 h. After cooling and dilution with EtOAc, the mixture was washed successively with 1 N HCl, saturated $NaHCO_3$, and brine, dried, and evaporated to afford 1,2-*O*-isopropylidene-5,6-*O*-(thiocarbonyl)-α-D-*ribo*-hexofuranose (51 g, 76%) as a colorless solid: mp 162°; R_f 0.65 (silica gel, $CHCl_3$/MeOH, 6:1); $[\alpha]_D$ −15.8 (*c* 1.0, MeOH); ^{1}H NMR δ 5.96 (d, 1H), 5.24 (ddd, $J_{4,5} = 2$ Hz, 1H), 4.75 (dd, $J = 7.6$ Hz, 1H), 4.67 (dd, $J = 8.9$, 8.9 Hz, 1H), 4.55–4.46 (m, 2H), 4.42 (d, $J = 3.2$ Hz, 1H), 1.46 (s, 3H), 1.30 (s, 3H). Anal. Calcd for $C_{10}H_{14}O_6S$: C, 45.8; H, 5.4. Found: C, 46.05, H, 5.4.

A solution of the foregoing thiocarbonate (26.5 g, 108 mmol) in dioxane (700 mL) was heated at reflux under N_2 and a solution of Bu_3SnH (100 mL, 377 mmol) and AIBN (7.4 g, 45 mmol) in toluene (1 L) was added over 2 h. The reaction mixture was cooled and evaporated, and the residue was purified by flash chromatography (silica, toluene/acetone, 6:5) to afford 1,2-*O*-isopropylidene-5-deoxy-α-D-*ribo*-hexofuranose (14.6 g, 71%) as a colorless solid: mp 91–92.5°; R_f 0.33 (silica, toluene/acetone 6:5); $[\alpha]_D$ −5.4 (*c* 0.5, MeOH); ^{1}H NMR ($CDCl_3$) δ 5.91 (d, $J = 3.8$ Hz, 1H), 4.55 (d, $J = 3.8$ Hz, 1H), 4.26 (ddd, $J = 7.2$, 7.2, 2.5 Hz, 1H), 4.14 (d, $J = 2.5$ Hz, 1H), 3.89 (ddd, $J = 10.7$, 6.0, 4.0 Hz, 1H), 3.74 (ddd, $J = 10.7$, 7.9, 4.0 Hz, 1H), 3.4 (br s, 1H), 2.65 (br s, 1H), 2.00 (m, 2H), 1.50 (s, 3H), 1.32 (s, 3H). Anal. Calcd for $C_9H_{16}O_5$: C, 52.9; H, 7.9. Found: C, 53.3; H, 7.6.



1,2:5,6-Di-*O*-isopropylidene-hex-3-ene-D-*threo*-1,2:5,6-tetraol [Conversion of a bis[*O*-(Methylthiothiocarbonyl)] Derivative into an Olefin with *N*-Ethylpiperidinium Hypophosphite Using Et_3B-O_2 Initiation].[199] A solution of 1,2:5,6-di-*O*-isopropylidene-3,4-bis[*O*-(methylthiothiocarbonyl)]-D-mannitol[239] (0.110 g, 0.25 mmol), EPHP (0.46 g, 2.49 mmol), and Et_3B (1 M in THF, 1.25 mL, 1.25 mmol) in degassed ethanol (5 mL) was stirred at rt and air was introduced by a syringe pump at 10 mL/h until TLC indicated the completion of the reaction. The reaction mixture was diluted with EtOAc, washed with H_2O, dried over $MgSO_4$, and evaporated. Flash chromatography of the residue (silica, hexane/EtOAc 9:1) gave the olefin (0.045 g, 79%), identical with an authentic sample.

TABULAR SURVEY

Individual entries within a table are arranged by increasing carbon count, which does not include protecting groups and simple alkyl groups on oxygen or nitrogen, or trialkylsilyl groups on acetylenic carbon. Other types of *C*-linked silyl groups are included in the carbon count. *O*- and *S*-substituents on aglycones in carbohydrate derivatives and *N*-substituents on nucleosides are included in the carbon count only when they are functionalized and/or are an integral part of the final target molecule. Within a given carbon count, entries are generally arranged according to increasing heteroatom count and molecular complexity. Like structures are grouped together: in the carbohydrates, furanosides precede pyranosides and within these subgroups, glucose derivatives precede galactose derivatives, etc.

The large number of secondary alcohol deoxygenation reactions necessitated the subdivision of Table 2. Commonly encountered substrates each have their own sub-table: carbohydrates include *C*-glycosides, nucleosides include all structural analogs, and steroids include all related structures. Other substrates are tabulated according to the number of contained rings, exclusive of those in protecting groups and irrespective of whether the rings are fused or separate. Each table includes any benzylic, allylic, or propargylic cases that fall within the table's structural category.

For all entries, the substrate column shows the *O*-thioacyl derivative and the Product column shows the corresponding deoxycompound plus any recorded coproducts. Yields without footnotes are for that single step. Footnotes are used when the reported yield is for either the two-step thioacylation-deoxygenation sequence or for a two- or more step sequence that may include the thioacylation step and does include the deoxygenation step plus additional, different steps, such as a protecting group introduction or removal. All yields are for the isolated product, unless a footnote indicates otherwise. Examples from the patent literature are limited to those from articles that provide a specific procedure plus appropriate characterization of the substrate and product.

Where available, the solvent, temperature, and time are included in the Conditions column or are given in data sub-tables associated with the entries. Proportions of reactants are provided when they form part of an optimization study, or when special conditions or reagents are employed.

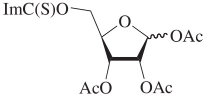
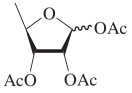
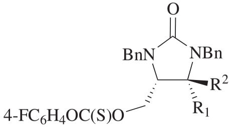
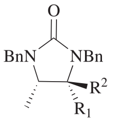
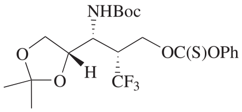
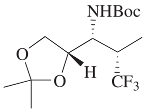
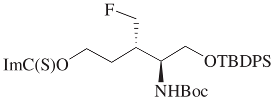
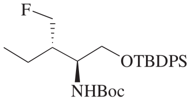
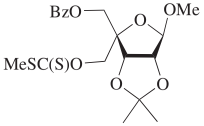
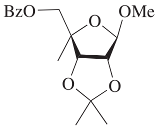
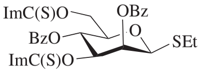
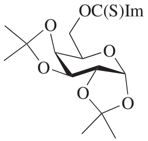
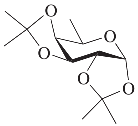
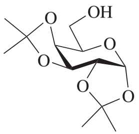
Except for the olefin formations from 1,2-bis(*O*-thioacyl) substrates in Table 5, fragmentation, rearrangement, and cyclization products are included only when they accompany the normal deoxygenation product, or when the latter can be formed using different conditions.

In addition to the *Journal of Organic Chemistry* standard abbreviations and acronyms, the following abbreviations are used in the tables:

ACCN	1,1′-azobis(1-cyanocyclohexane)
ACVA	4,4′-azobis(4-cyanopentanoic acid)
AMBN	2,2′-azobis(2-cyanobutane)
AMHP	2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]
Alloc	allyloxycarbonyl
BOM	benzyloxymethyl
Bs	benzenesulfonyl
BTAH	benzyltriethylammonium hydroxide
Cbe	ethoxycarbonyl
4-ClBn	4-chlorobenzyl
CTAB	cetyltrimethylammonium bromide
DCB	2,6-dichlorobenzyl
DEIPS	diethylisopropylsilyl
DMIPS	dimethylisopropylsilyl
DMTr	dimethoxytrityl; phenyl bis(4-methoxyphenyl)methyl
DPC	*N*, *N*-diphenylcarbamoyl
EPHP	1-ethylpiperidinium hypophosphite
eq	equivalents
ia	inverse addition
Im	imidazol-1-yl
2-ME	2-methoxyethanol
MMTr	monomethoxytrityl; diphenyl (4-methoxyphenyl)methyl
MTM	methylthiomethyl
NEP	*N*-ethylpiperidine
o/n	overnight
9-PhFl	9-phenylfluoren-9-yl
PhthN	phthalimido
PMHS	poly(methylhydrosiloxane)
PMP	4-methoxyphenyl
PNP	4-nitrophenyl
SEM	(2-trimethylsilylethoxy)methyl

SM	starting material
TBDPS	*tert*-butyldiphenylsilyl
TBHN	*tert*-butyl hyponitrite
TBAH	tetra-*n*-butylammonium hydroxide
TBPB	tetra-*n*-butylphosphonium bromide
TCE	2,2,2-trichloroethoxycarbonyl
TMSE	2-(trimethylsilyl)ethyl
TMTHF	2,2,5,5-tetramethyltetrahydrofuran
m-tol	3-methylphenyl
p-tol	4-methylphenyl
V-70	2,2′-azobis(2-cyano-4-methoxybutane)

TABLE 1. PRIMARY ALCOHOLS

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		$(Bu_4N)_2S_2O_8$, HCO_2Na, $NaHCO_3$, DMF, 65°, 0.5 h	 (40)	224
		Bu_3SnH, AIBN, toluene, reflux	 R^1 R^2 CH_2OH H (57) H CO_2Me (47)[a]	368
C_6		Bu_3SnH (slow addition), xylenes, reflux, 24 h	 (65)	369
		Bu_3SnH, AIBN, toluene, reflux, 2 h	 (65)	370
		$(TMS)_3SiH$, ACCN, toluene, 100°, 15 h	 (28)[b]	371
		Bu_3SnH, AIBN, toluene, reflux	 (45)	372
		Bu_3SnH, AIBN, toluene, reflux	 **I** (31) +  (57)	72

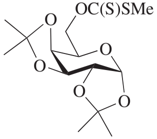
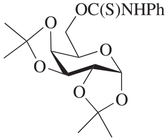
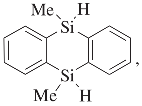
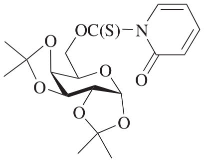
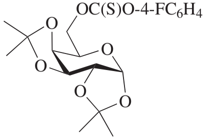
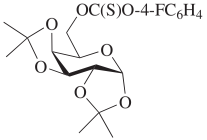
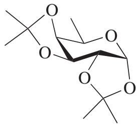
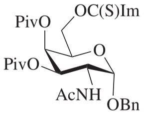
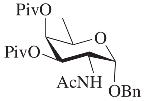
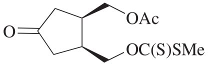
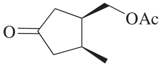
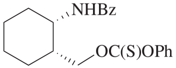
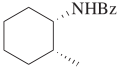
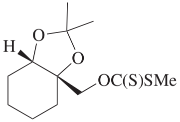
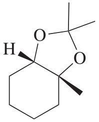
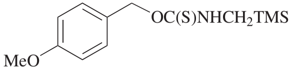
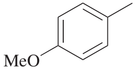
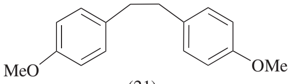
	$Bu_2P(O)H$, AIBN, toluene, reflux, 32 h	**I** (80)	205
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), DMF, 65°, 15 min	**I** (86)	211
	$(TMS)_3SiH$, AIBN, benzene, reflux, 8 h	**I** (85)	39
	 AIBN, benzene, reflux, 3 h	**I** (40)	373
	Bu_3SnH, AIBN, toluene, reflux, 1–2 h	**I** (62)	74
	MH (2 eq), initiator (*x* eq, added in portions), toluene, reflux	**I** MH / Initiator / *x* / Time (h) / **I** $PhSiH_3$ / AIBN / 0.8 / 1.25 / (88) Ph_3SiH / Bz_2O_2 / 2.2 / 3.75 / (88)	367
	Et_3SiH (neat), Bz_2O_2 (0.8 eq, added in portions), reflux, 2 h	**I** (96)^c	367

TABLE 1. PRIMARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$R_2P(O)H$ (*x* eq), amine (*y* eq), initiator (*z* eq, added slowly), dioxane, reflux	 **I**	

$R_2P(O)H$	*x*	Amine	*y*	Initiator	*z*	Time (h)	**I**	Refs.
$(MeO)_2P(O)H$	5	—	—	Bz_2O_2	0.6	1.5	$(90)^c$	112
H_3PO_2	10	Et_3N	11	AIBN	0.66	2	$(91)^c$	194
H_3PO_2	10	NEP	10	AIBN	1.16	2.5	$(91)^c$	194
H_3PO_2	10	Bu_3N	11	AIBN	0.66	2.5	$(96)^c$	193

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (30)	374
C_7 	Et_3SiH, $(t\text{-}Bu)_2O_2$, $n\text{-}C_{12}H_{25}SH$	 (65)	223
	Bu_3SnH, AIBN, benzene, reflux, 4.5 h	 (51)	375
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (50)	376
	Et_3SiH, $(t\text{-}Bu)_2O_2$ or Bz_2O_2, 140°, sealed tube, 21–48 h	 (39) +  (21)	75

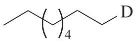
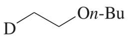
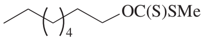
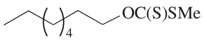
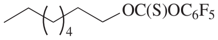
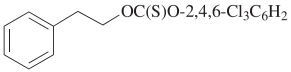
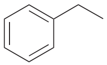
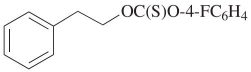
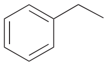
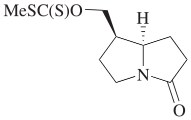
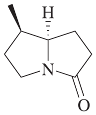
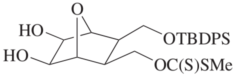
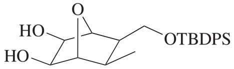
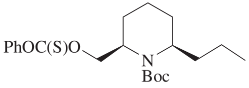
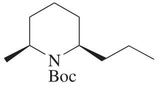
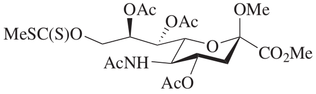
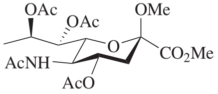
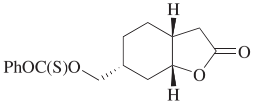
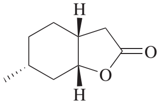
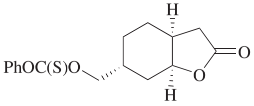
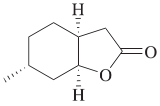
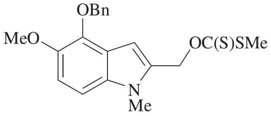
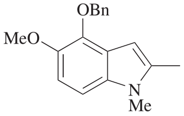
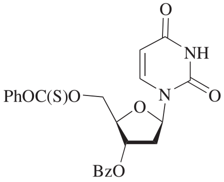
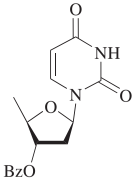
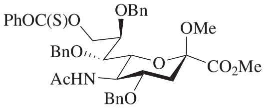
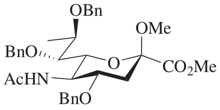
C_8		Bu_3SnD, $(t\text{-}Bu)_2O_2$, decane, 120°	 (53)^c +  (42)^c	30
		Et_3SiH (2 eq), $t\text{-}C_{12}H_{25}SH$ (0.02 eq), 1,1-di-(*tert*-butylperoxy)-cyclohexane (*x* eq), cyclohexane, sealed tube, 115°	 **I** *x* | Time (h) 0.02 | 1 | (63)^d 0.05 | 4 | (82)^d	175, 170
		Bu_3SnD, AIBN, toluene, 80°	 (23)	30
		Bu_3SnH, AIBN, toluene, reflux, 0.25 h	 (97)	35
		Bu_3SnH, AIBN, toluene, reflux, 10 min	 (100)	35
		Ph_2SiH_2, Et_3B (0.25 eq), air (added slowly), benzene, reflux, 30 min	 (80)	35
		Bu_3SnH, AIBN, benzene, reflux, 3.5 h	 (61)	218
		Bu_3SnH, AIBN, toluene, reflux	 (88)^b	377, 378
C_9		Bu_3SnH, AIBN	 (48)	379

TABLE 1. PRIMARY ALCOHOLS (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		Bu_3SnH, xylene, 120°, 2.5 h	 (—)	380
		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (88)	219
		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (73)	219, 381
		Bu_3SnH, AIBN, benzene, reflux, 5 h	 (61)	382
		Bu_3SnH, AIBN, toluene	 (—)	383
		Bu_3SnH, AIBN, toluene, 80°, 1 h	 (39)[a]	75

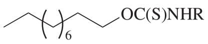
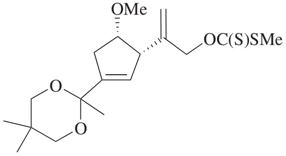
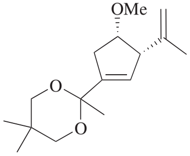
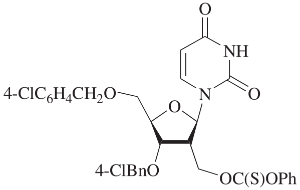
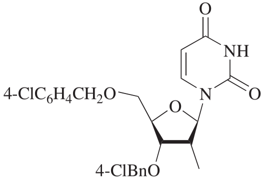
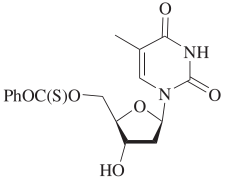
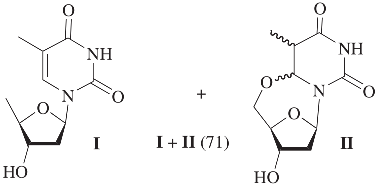
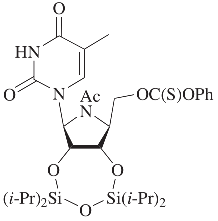
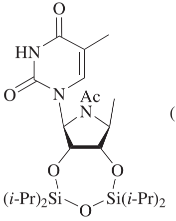
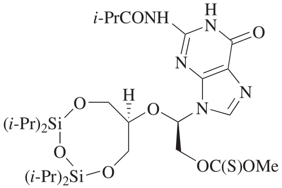
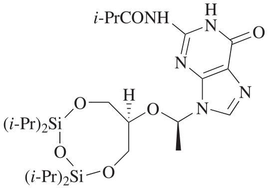
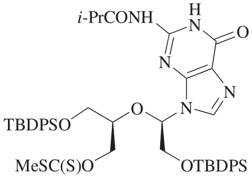
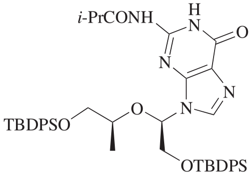
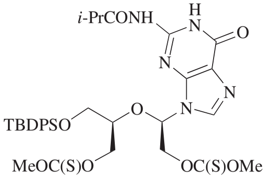
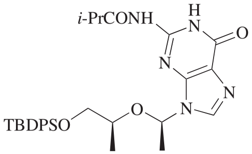
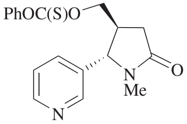
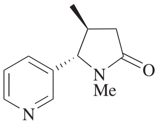
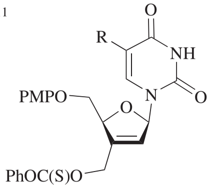
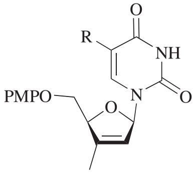
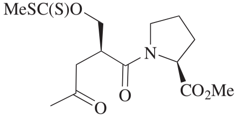
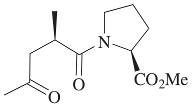
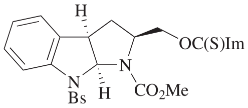
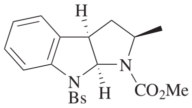
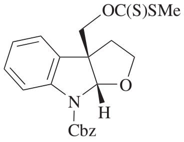
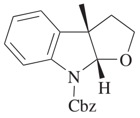
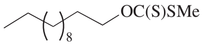
C$_{10}$						
	Et_3SiH, (t-Bu)$_2O_2$ or Bz_2O_2, benzene, 140°, sealed tube		R	Isolated		75
			Et	(70)	(95)^d	
			Ph	(67)	(95)^d	
			Bn	(6)	(—)^d	
			CH_2TMS	(88)	(—)^d	
	Bu_3SnH, AIBN, benzene, reflux			(73)^b		221
	Bu_3SnH, AIBN, toluene, reflux, 2 h			(39)^a		385
	Bu_3SnH, AIBN, benzene, reflux, 1.5 h	 **I** + **II** **I** + **II** (71)				26
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h			(68)		386

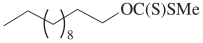
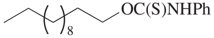
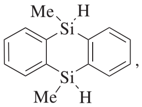
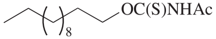
TABLE 1. PRIMARY ALCOHOLS (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		Bu_3SnH (5 eq), AIBN, dioxane, reflux, 1.5 h	 (57)	387
		Bu_3SnH (5 eq), AIBN, dioxane, reflux, 2 h	 (43)	387
		Bu_3SnH (5 eq), AIBN, dioxane, reflux, 1 h	 (5)[b]	387
		$(TMS)_3SiH$, AIBN, toluene, 90°, 3 h	 (76)	388

C_{10-11}				
	Bu_3SnH, AIBN, toluene, reflux, 2 h		R: H (67) Me (75)	389, 390
C_{11}				
	Bu_3SnH, AIBN, toluene, 80°, 8 h		(70)	391
	Bu_3SnH, AIBN, C_6H_5Cl, reflux, 0.5 h		(68)	222
	Bu_3SnH, AIBN, toluene, 80°		(29)	392
C_{12}				
	$Bu_2P(O)H$, initiator, solvent, reflux	 **I** + SM (**II**)		205

Initiator	Solvent	Time (h)	**I**	**II**
$(t\text{-Bu})_2O_2$	dioxane	48	$(11)^d$	(85)
AIBN	dioxane	48	$(36)^d$	(60)
AIBN	xylene	32	$(87)^d$	(—)

TABLE 1. PRIMARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	$Ph_2P(O)H$, $(t\text{-}Bu)_2O_2$, reflux	 **I** + SM (**II**) Solvent / Time (h) / **I** / **II** dioxane / 40 / $(69)^d$ / (25) xylene / 32 / $(90)^d$ / (—)	206
	Me_3B (2.5–4.0 eq), H_2O (5 eq), O_2 (0.8 eq, as air, added slowly), benzene, rt	**I** (42)	38
	Me_3B (2.5–4.0 eq), D_2O (20 eq), O_2 (0.8 eq, as air, added slowly), benzene, rt	 $(51)^d$	38
	$(TMS)_3SiH$, AIBN, benzene, reflux, 5 h	 **I** $(84)^d$	39
	, AIBN, benzene, reflux, 3 h	**I** $(64)^d$	76, 373
	Bu_3SnH, AIBN, 140°, 20 min	**I** $(51)^d$	77
	Ph_3SiH, Et_3B, O_2, benzene, reflux, 10 min	**I** $(83)^d$	77
	Bu_3SnD, AIBN, benzene, reflux, 30 min	 $(58)^d$	77

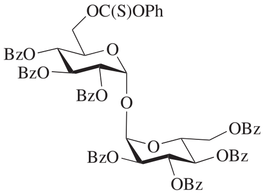
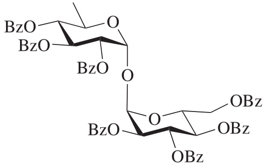
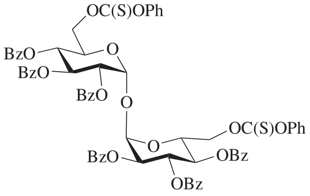
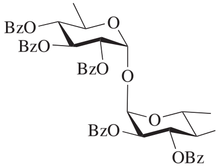
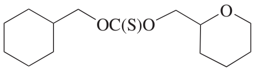
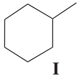
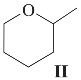
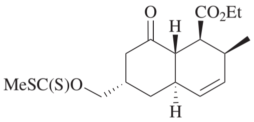
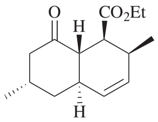
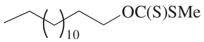
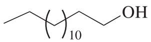
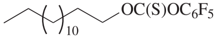
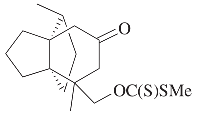
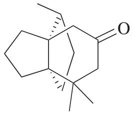
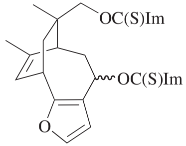
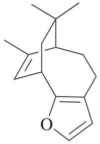
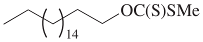
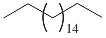
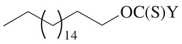
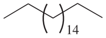
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (60)^b	393
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (32)^b	393
C_{13}			
	Bu_3SnH, AIBN, *t*-BuC_6H_5, reflux	 (—) +  (—) **I** **II** **I**:**II** = 1.76:1	30
	Bu_3SnH (7 eq), *p*-cymene, 150°, 18 h	 (63)	394
C_{14}			
	$Ph_2SiHSiHPh_2$ (1.1 eq), AIBN (0.3 eq), EtOAc, reflux, 16 h	 (51) **I**	186
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), DMF, 50°, 30 min	**I** (100)	211
	Bu_3SnH, Et_3B, benzene, rt, 20 min	**I** (18) +  (30)	91

TABLE 1. PRIMARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	Bu_3SnH, AIBN, benzene, reflux, 20 min	**I** (90)^{a,d}	35
	Bu_3SnH, AIBN, toluene, reflux, 5 min	**I** (95)^{a,d}	35
C_{15}			
	Bu_3SnH, AIBN, benzene	 (84)	395
	Bu_3SnH, AIBN, toluene, reflux	 (31)	396
C_{18}			
	R_3SiH (x eq), dicumyl peroxide (0.04 eq), t-$C_{12}H_{25}SH$ (y eq), octane, reflux	 R x y Time (h) Et 2 0 4 (60) Et 2 0.02 4 (80) n-Pr 4 0.02 2 (79)	175, 170
	MH, solvent, reflux, 11–14 h	 Y MH Solvent Im Bu_3SnH xylene (81) Ph Bu_3SnH xylene (84) SMe Bu_3SnH xylene (51) SMe Ph_3SnH xylene (31) SMe Bu_3SnH p-cymene (71) SMe Ph_3SnH p-cymene (37)	59

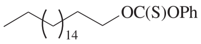
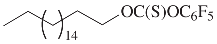
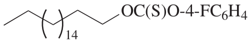
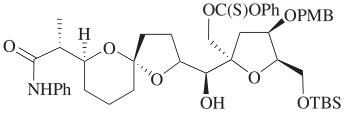
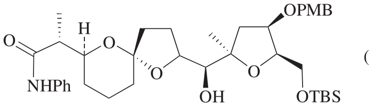
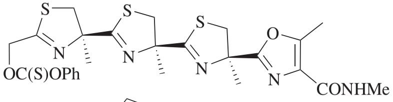
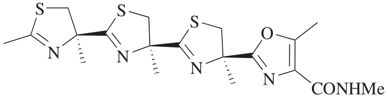
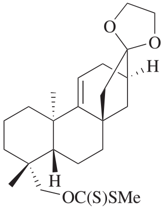
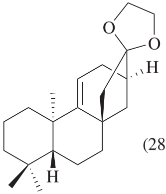
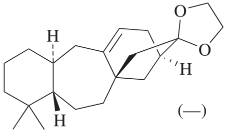
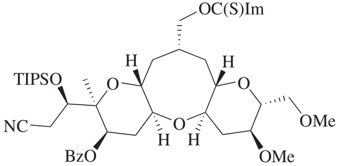
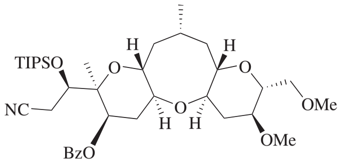
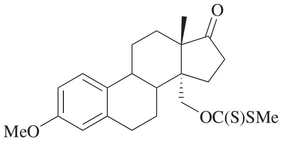
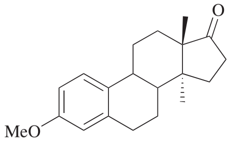
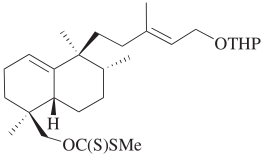
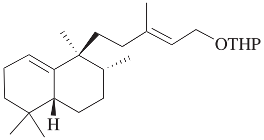
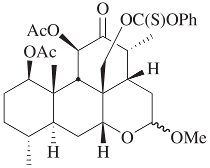
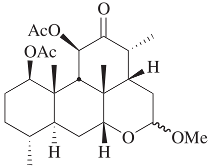
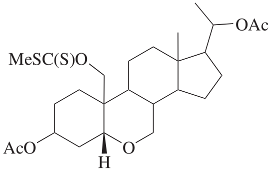
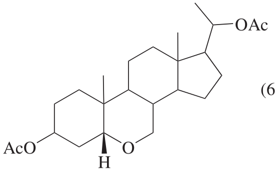
C_{18}			
	PMHS (5 eq), $(Bu_3Sn)_2O$ (0.12 eq), BuOH (5.5 eq), AIBN, toluene, 80–100°	 **I** (66)	92
	Bu_3SnH, AIBN, toluene, 80–100°	**I** (68)	92
	Bu_3SnH, AIBN, toluene, reflux, 12 min	**I** (86)[d]	35
	Ph_2SiH_2 (1.1 eq), Et_3B (0.25 eq), air (added slowly), benzene, reflux, 0.5 h	**I** (87)[c]	35
	$PhSiH_3$ (2 eq), AIBN (1 eq, added in portions), toluene, reflux, 1.25 h	**I** (100)[d]	367
	$(MeO)_2P(O)H$ (5 eq), Bz_2O_2 (0.8 eq, added in portions), dioxane, reflux, 2 h	**I** (91)	194, 112
	Bu_3SnH, AIBN, xylenes, 160°	 (72)	397
	$(TMS)_3SiH$, AIBN, toluene, 110°, 1 h	 (63)	398
C_{19}			
	Bu_3SnH, AIBN	 (28)[b] +  (—)	399

TABLE 1. PRIMARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19} 	Bu_3SnH, AIBN, toluene, 95°, 5 min	 (80)[a]	220
C_{20} 	Bu_3SnH	 (—)	400
	Bu_3SnH, AIBN, toluene, reflux, 20 min	 (31)	401
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (69)	402, 403
	Bu_3SnH, xylene, reflux, 16 h	 (63)	404

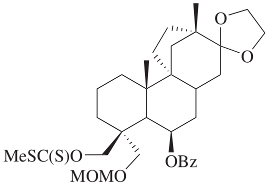
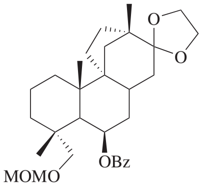
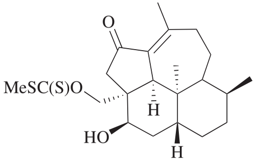
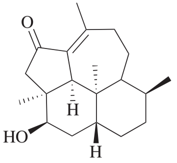
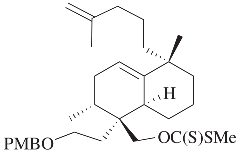
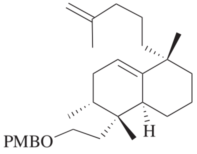
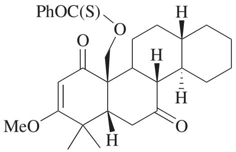
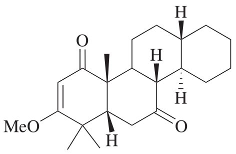
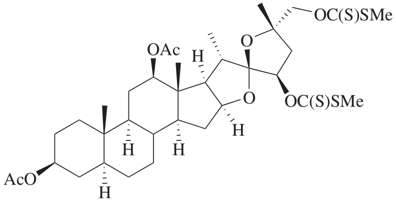
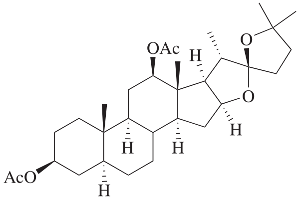
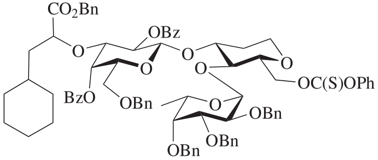
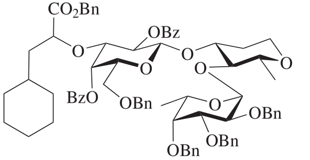
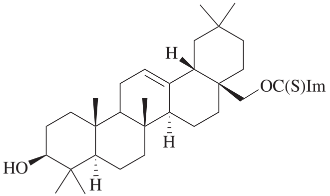
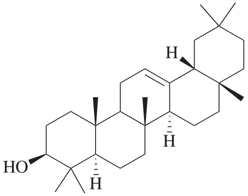
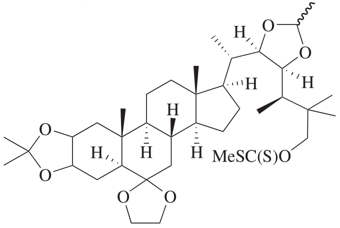
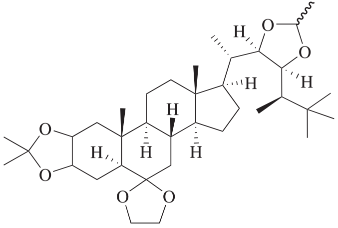
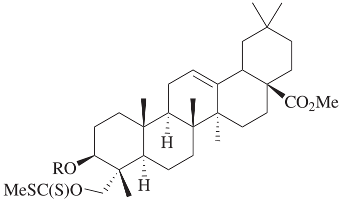
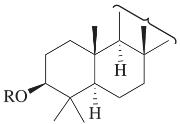
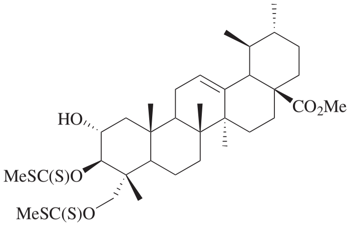
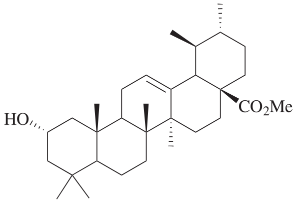
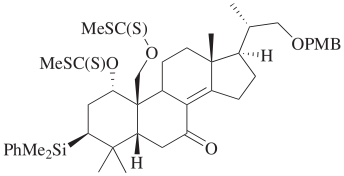
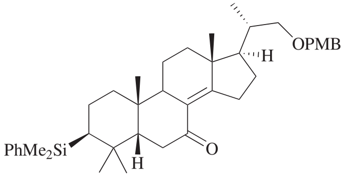
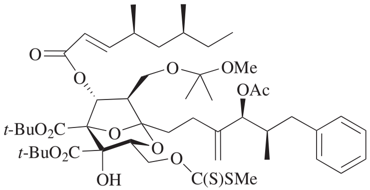
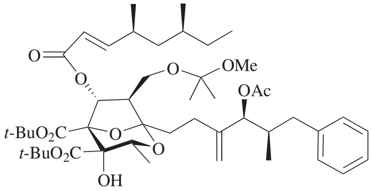
C$_{20}$		Bu$_3$SnH, AIBN, benzene, reflux, 1 h	 (63)[b]	405
		(TMS)$_3$SiH, AIBN, toluene, reflux	 (38)	406
C$_{21}$		Ph$_2$SiH$_2$, Bz$_2$O$_2$, *o*-xylene, reflux, 40 min	 (81)[b]	407
C$_{22}$		Bu$_3$SnH, AIBN, toluene, reflux	 (99)	408
C$_{27}$		(TMS)$_3$SiH	 (85)[b]	409

TABLE 1. PRIMARY ALCOHOLS (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27}		Bu_3SnH, AIBN, benzene, reflux	 (48)	410
C_{29}		Bu_3SnH, xylene, reflux, 2 h	 (40)	59
		Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (74)	411
C_{30}		MH, Bz_2O_2 (added in portions), reflux	 **I** R MH Solvent H Ph_2SiH_2 toluene (49) H $PhSiH_3$ toluene (55) Ac $PhSiH_3$ toluene (56) Ac Ph_2SiH_2 *o*-xylene (75) Bz Ph_2SiH_2 *o*-xylene (91) Bz Ph_3SiH *o*-xylene (87)	35
		Bu_3SnH, *p*-cymene, reflux, 2 h	**I** (R = H) (65)	59

		Bu$_3$SnH, toluene, reflux, 2 h		(82)	412
C_{32}		(TMS)$_3$SiH, AIBN, toluene, reflux		(50)	413
C_{34}		Bu$_3$SnH, xylene, reflux		(62)[a]	414

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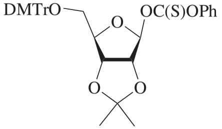
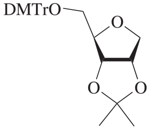
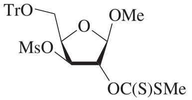
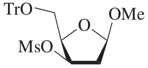
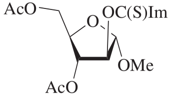
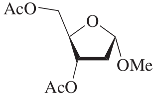
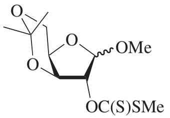
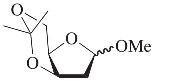
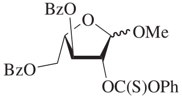
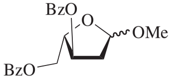
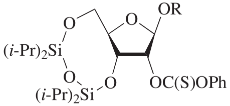
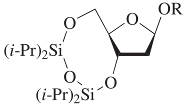
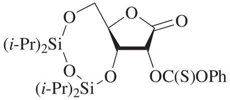
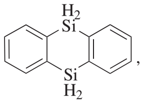
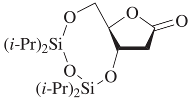
[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

[c] The yield was determined by NMR.

[d] The yield was determined by GC.

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		Bu_3SnH, AIBN	 (50)	415
		Bu_3SnH, AIBN, toluene, reflux, 2 h	 (100)	416
		H_3PO_2, Et_3N, AIBN (0.6 eq), DME, reflux, 2 h	 (60)	417
		Bu_3SnH, AIBN, xylene, reflux, 5 h	 (—)	418
		Bu_3SnH, AIBN, toluene, 80°, 3 h	 $(53)^{a}$	419
		Bu_3SnH, AIBN, toluene, 75–80°	 R Time (h) Me 3 $(62)^{b}$ $4\text{-}O_2NC_6H_4$ o/n (63)	34, 420
		, AIBN, cyclohexane, 80°	 (96)	187

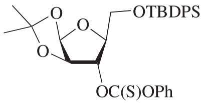
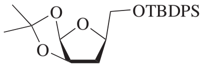
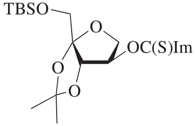
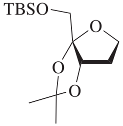
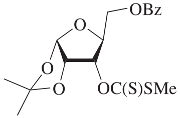
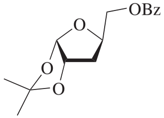
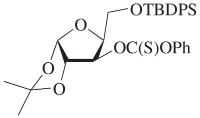
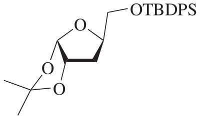
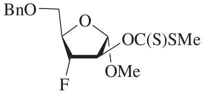
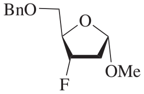
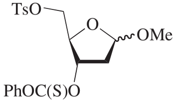
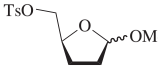
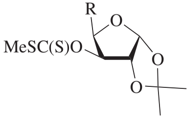
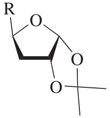
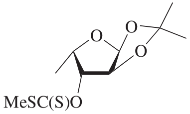
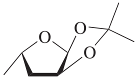
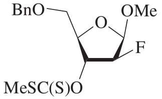
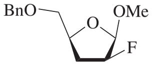
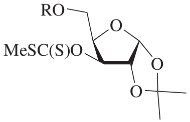
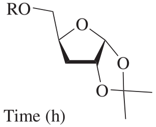
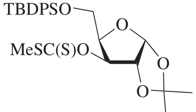
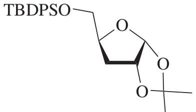
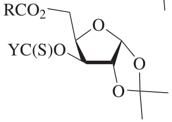
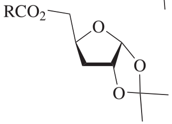
C$_5$ 	Bu$_3$SnH, AIBN, toluene, 90°, 6 h		(95)	421
	Bu$_3$SnH, toluene, reflux		(72)	422
	Bu$_3$SnH, AIBN, benzene, reflux, 4 h		(68)^a	423
	Bu$_3$SnH, AIBN, toluene, 80°, 1 h		(—)	424
	Bu$_3$SnH, AIBN, toluene, reflux, 5 h		(62)^a	425
	Bu$_3$SnH, AIBN, benzene, reflux, 2 h	 **I**	(83)	426
	Bu$_3$SnH, AIBN, toluene	**I** (73)		427
C$_{5-9}$ 	Bu$_3$SnH, AIBN, toluene, reflux, 1–12 h	 R		
		Me	(52–61)	428, 429
		Et	(50)^a	429
		n-C$_5$H$_{11}$	(64)^a	429

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	Bu_3SnH, toluene	 (96)	430
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 **I** (86)	431
	$(n\text{-}C_{11}H_{23}CO_2)_2$, *i*-PrOH, reflux	**I** (77)	212
	Diglyme (traces of peroxides), 100°, 4 h	**I** (42)	212
	Bu_3SnH, initiator, solvent		

R	Initiator	Solvent	Temp (°)	Time (h)		Refs.
Me	AIBN	—	100	—	(60)	432
Tr	AIBN	toluene	reflux	1	(78)	433
Tr	—	toluene	reflux	60	(82)	434
TBDPS	AIBN	toluene	reflux	5	(84)	435
TBDPS	AIBN	toluene	80	1	(77)	424
Ts	AIBN	—	—	—	(—)	436

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), Na_2CO_3 (8 eq), DMF, 65°, 15 min	 (75)	211
	Bu_3SnH, AIBN, toluene		

R	Y	Temp (°)	Time (h)		
Me	Im	reflux	2	(95)	437
MeO	Im	reflux	2.5	(58)	438
Ph	PhO	100	—	(63)	439
$4\text{-}MeC_6H_4$	Im	—	—	(100)	440

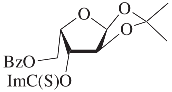
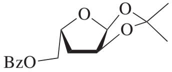
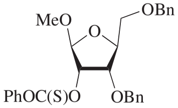
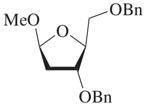
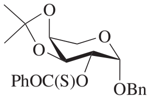
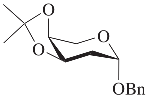
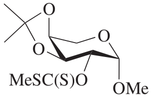
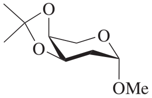
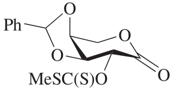
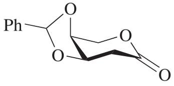
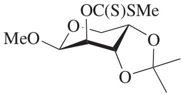
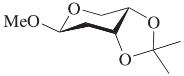
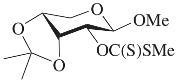
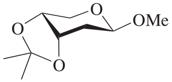
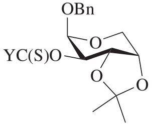
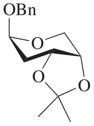
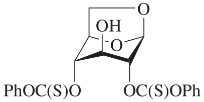
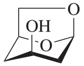
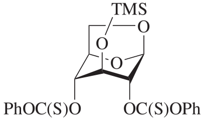
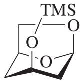
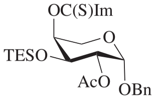
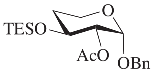
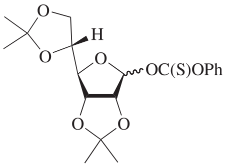
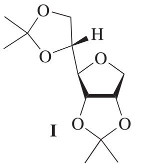
	$(TMS)_3SiH$, AIBN, toluene, reflux, 1 h		(92)	441
	Bu_3SnH, AIBN, toluene, reflux, 1 h		(74)	442
	Bu_3SnH, AIBN, toluene, reflux, 1.25 h		(53)[b]	443
	Bu_3SnH, AIBN, toluene		(66)	444
	Bu_3SnH, toluene, reflux, overnight		(85)	445
	Ph_2SiH_2, AIBN, dioxane, reflux, 17 h		(81)[b]	174
	Bu_3SnH, AIBN, benzene, reflux, 16 h		(74)	446

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 Y MeS (85) PhNH (55) Im (36) PhO (59)	447
		$(TMS)_3SiH$, AIBN, toluene, reflux, 0.5 h	 **I** (87)	448
		Ph_2SiH_2, AIBN, toluene, reflux	**I** (48–60)	448
		Ph_2SiH_2, AIBN, toluene, reflux	**I** (46)	449
		$(TMS)_3SiH$, AIBN, toluene, reflux, 1.5 h	**I** (86)	449
		Bu_3SnH, AIBN, toluene, reflux, 3 h	**I** (60)	449
		Ph_2SiH_2, AIBN, toluene, reflux, 0.5 h	 (85)[b]	448
		Bu_3SnH, toluene, reflux	 (85)	450
C_6		PMHS (5 eq), $(Bu_3Sn)_2O$ (0.075 eq), BuOH (5.5 eq), AIBN, toluene, 80–100°	 **I** (63)	92
		Bu_3SnH, AIBN, toluene, 80–100°	**I** (72)	92

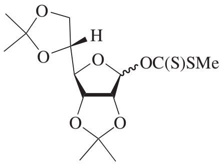
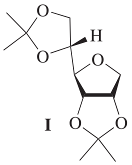
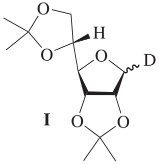
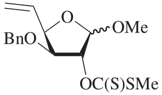
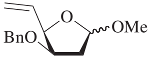
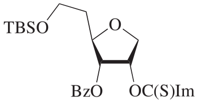
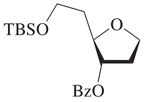
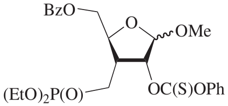
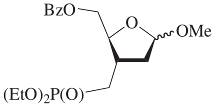
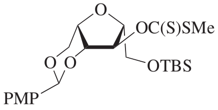
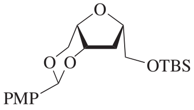
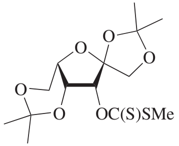
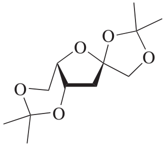
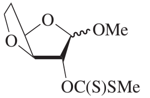
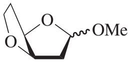
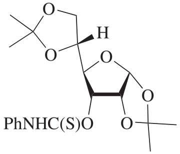
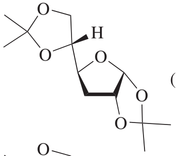
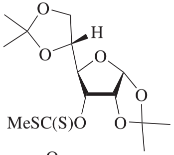
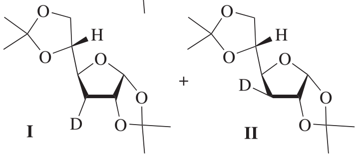
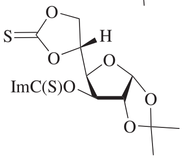
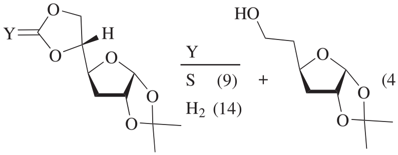
C_6		$R_2SiHSiHR_2$ (1.1 eq), initiator (*x* eq), EtOAc, reflux, 16 h	 **I**	R | Initiator | *x* Ph | AIBN | 0.3 (86) Ph | Et_3B | 0.6 (80) $4\text{-}FC_6H_4$ | AIBN | 0.3 (71)	186
		Me_3B (2.5–4.0 eq), H_2O (5 eq), O_2 (0.8 eq as air, added slowly), benzene, rt	**I** (91)		38
		Me_3B (2.5–4.0 eq), D_2O (20 eq), O_2 (0.8 eq as air, added slowly), benzene, rt	 **I**	(68)	38
		Bu_3B (5.0 eq), D_2O (20 eq), O_2 (0.8 eq as air, added slowly), benzene, rt	**I** (66)		38
		Bu_3SnH, toluene, reflux, 5 d		(65)	451
		Bu_3SnH, AIBN, toluene, reflux, 3.5 h		(88)	452
		Bu_3SnH, AIBN, toluene, 75°, 3 h		$(72)^b$	453
		Bu_3SnH		(—)	454

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	*i*-PrOH, (n-$C_{11}H_{23}CO_2)_2$, collidine, reflux	 (81)	32
	Bu_3SnH, AIBN, toluene, reflux, 8 h	 (85)	455
	$(TMS)_3SiH$, AIBN, benzene, reflux, 8 h	 (82)	39
	Bu_3SnD, AIBN, benzene, reflux, 10 h	 **I** + **II** **I + II** (100); **I**:**II** = 87:13	39
	Bu_3SnD, toluene, reflux, 18 h	**I + II** (—), **I**:**II** = 85:15	46
	Bu_3SnH, toluene	 Y S (9) H_2 (14) + (41)	456

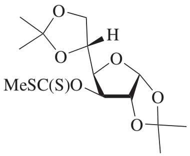
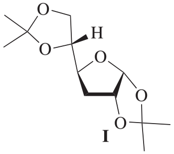
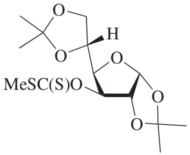
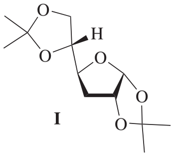
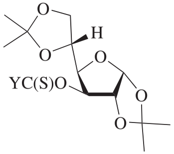
	Bu_3SnH, initiator, toluene, reflux	 **I**	Initiator	Time (h)		
			none	18	(85)	1
			none	4–7	(75)	56
			none	16	(62)[b]	457
			none	3	(85)	89
			AIBN	—	(75)	175
			AIBN	—	(46)	429
	Ph_3SiH, TBHN, dioxane, 60°, 2.5 h	**I** (90)				176
	Et_3SiH, $t\text{-}C_{12}H_{25}SH$, $(t\text{-Bu})_2O_2$, octane, reflux, 6 h	**I** (60)				175
	$PhSiH_3$, AIBN, toluene, reflux, 80 min	**I** (100)[c]				172
	$PhSiH_3$ (2 eq), Bz_2O_2 (1 eq, added in portions), toluene, reflux, 3.5 h	**I** (96)[c]				367
	Et_3SiH (neat), Bz_2O_2 (1 eq, added in portions) reflux, 2.5 h	**I** (89)[c]				367
	$R_2SiHSiHR_2$ (1.1 eq), AIBN (0.3 eq), EtOAc, reflux, 16 h	**I** R — **I** Ph (89) 4-FC_6H_4 (81) 4-MeOC_6H_4 (47)				186
	Ph(Me)SiHSiH(Me)Ph (1.1 eq), AIBN (0.3 eq), EtOAc, reflux, 16 h	**I** (85)				186
	Et_3B (5 eq), high dilution, slow addition of substrate and O_2, $ClCH_2CH_2Cl$, rt, 1.5 h	**I** (57)				216

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	R_3P•BH_3, AIBN, solvent, reflux, 2 h	 **I** R / Solvent *i*-PrO / benzene / $(23)^c$ MeO / benzene / $(31)^c$ Et_2N / benzene / $(42)^c$ Ph / benzene / $(44)^c$ Ph / dioxane / $(90)^c$ TMSO / dioxane / $(85)^c$ Bu / benzene / $(80)^c$ Bu / dioxane / $(89)^c$	110
	$R_2P(O)H$, AIBN, dioxane, reflux	**I** R / Time (h) / **I** Bu / 24 / (93) Ph / 32 / (80)	205 206
	EPHP (5 eq), ACVA (0.75 eq), CTAB (2 eq), H_2O, 80°, 9 h	**I** (81)	199
	$[n\text{-}C_{16}H_{33}NMe_3]^+$ $H_2PO_2^-$ (3 eq), ACVA (0.5 eq), H_2O, reflux, 7 h	**I** (88)	201
	$R_2P(O)H$ (5 eq), R_3N (*x* eq), initiator (*y* eq, added in portions), solvent, reflux	**I**	194

Y	$R_2P(O)H$	R_3N	*x*	Initiator	*y*	Solvent	Time (h)	**I**
$4\text{-}FC_6H_4O$	$(MeO)_2P(O)H$	—	0	Bz_2O_2	0.6	dioxane	1.5	$(92)^c$
$4\text{-}FC_6H_4O$	$(EtO)_2P(O)H$	—	0	Bz_2O_2	0.4	dioxane	1	$(91)^c$
$4\text{-}FC_6H_4O$	H_3PO_2	Et_3N	5.5	AIBN	0.4	dioxane	0.75	$(100)^c$
$4\text{-}FC_6H_4O$	H_3PO_2	NEP	6.0	AIBN	0.33	dioxane	1	$(99)^c$
C_6F_5O	$(MeO)_2P(O)H$	—	0	Bz_2O_2	0.8	dioxane	2	$(100)^c$
C_6F_5O	H_3PO_2	Et_3N	5.5	AIBN	0.33	dioxane	1	$(39)^c$
MeS	$(MeO)_2P(O)H$	—	0	Bz_2O_2	1.6	dioxane	1.5	$(97)^c$
MeS	$(MeO)_2P(O)H$	—	0	Bz_2O_2	1.0	toluene	2.5	$(92)^c$
MeS	H_3PO_2	Et_3N	5.5	AIBN	0.4	dioxane	0.75	$(84)^c$
MeS	H_3PO_2	Et_3N	11	AIBN	0.5	dioxane	0.75	$(91)^c$
MeS	H_3PO_2	NEP	5.0	AIBN	0.33	dioxane	1	$(87)^c$

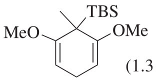
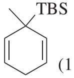
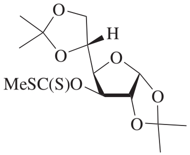
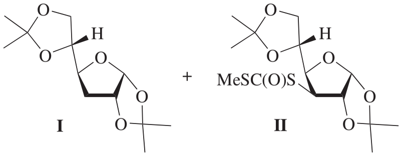
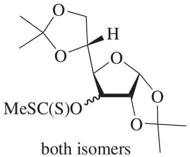
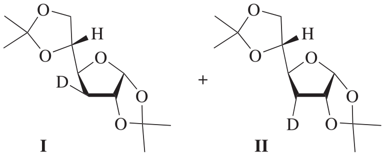
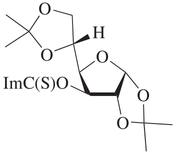
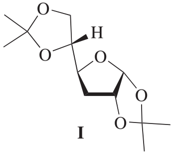
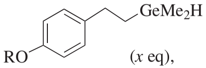
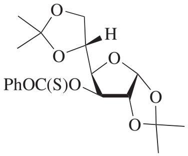
	 (1.3 eq), AIBN (0.3 eq), hexanes, reflux, 18 h	**I** Y / **I** PhO (91) MeS (70)	209
	 (1.3 eq), TBHN (0.3–1.5 eq), hexanes, reflux, 4 h	**I** Y / **I** PhO (83) MeS (68)	209
	$(n\text{-}C_{11}H_{23}CO_2)_2$, collidine, reflux Solvent / **I** / **II** *i*-PrOH (70) (20) benzene (12) (70)		32
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), Na_2CO_3 (8 eq), DMF, 65°, 0.25 h	**I** (75)	211
	Me_3B (2.5–4.0 eq), H_2O (5 eq), O_2 (0.8 eq as air, added slowly), benzene, rt	**I** (63)	38
 both isomers	Bu_3SnD, toluene, reflux, 18 h	 **I** + **II** (—), **I**:**II** = 85:15	46, 458
	Me_3B (20–50 eq), D_2O (20 eq), O_2 (0.8 eq as air, added slowly), benzene, rt	**I** + **II** (60), **I**:**II** = —	38

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Bu_3SnH, toluene, reflux	 **I** (74)	72
	Et_3B (5 eq), high dilution, slow addition of substrate and O_2, DCE, rt, 1.5 h	**I** (80)	216
	Bu_3GeH, ACCN, MeCN, reflux, 1.5 h	**I** (87)	189
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), Na_2CO_3 (8 eq), DMF, 65°, 15 min	**I** (97)	211
	$Ph_2SiHSiHPh_2$ (1.1 eq), AIBN (0.3 eq), EtOAc, reflux, 16 h	**I** (92)	186
	 (*x* eq), ACCN, toluene, reflux, 2 h	**I** R / *x* / I H / 3.0 / (94) Bn / 3.3 / (91)	190
	Matrix-bound $GeMe_2H$ (1.3 eq), ACCN, toluene, reflux, 7 h	**I** (36)	190
	Polystyrene-linked Bu_2SnH, AIBN, $(MeO)_3SiH$ (15 eq), BuOH (16.5 eq), toluene, reflux, 36 h	**I** (74)	156

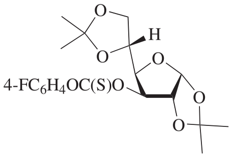
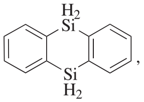
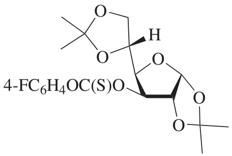
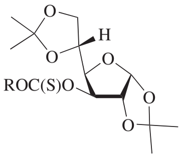
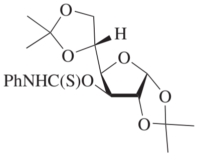
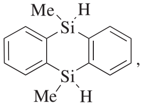
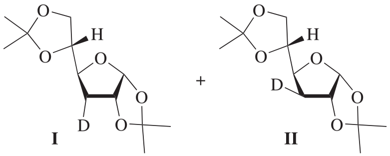
	Polystyrene linked-Bu_2SnH, AIBN, toluene, 80°	**I** (84)	104
	Polystyrene linked-Bu_2SnH, AIBN, toluene, 75°, 3 h	**I** (87)	34
	Bu_3SnH, AIBN, toluene, 80–100°	**I** (79)	92, 459
	$(TMS)_3SiH$, AIBN, toluene, 80°, 2 h	**I** (81)	90
	PMHS (5 eq), $(Bu_3Sn)_2O$ (cat.), BuOH (5.5 eq), AIBN, toluene, 80–100°	**I** (75)	92, 459
	 , AIBN, cyclohexane, reflux, 3 h	**I** (91)	187
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), Na_2CO_3 (8 eq), DMF, 65°, 20 min	**I** (90)	211
	$PhSiH_3$ (2 eq), Bz_2O_2 (0.8 eq, added in portions), toluene, reflux, 1.25 h	**I** (100)^c	367
	Ph_3SiH (2 eq), Bz_2O_2 (2.6 eq, added in portions), toluene, reflux, 4.5 h	**I** (100)^c	367
	Et_3SiH (neat), Bz_2O_2 (1 eq, added in portions) reflux, 2.5 h	**I** (96)^c	367

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	MH, Et_3B, O_2, benzene, rt, 40 min	**I** MH — **I** Ph_2SiH_2 (94) $(TMS)_3SiH$ (94)	173
	H_3PO_2, AIBN, R_3N, dioxane, reflux	**I** R_3N — **I** Et_3N $(100)^c$ Bu_3N $(98)^c$ DABCO $(100)^c$	193
	Bu_3SnH, AIBN, toluene, reflux, 5–15 min	**I** R — **I** Ph $(72)^c$ 2,4,6-$Cl_3C_6H_2$ $(100)^c$ C_6F_5 $(100)^c$	68
	$(TMS)_3SiH$, AIBN, benzene, reflux, 2 h	**I** (99)	39
	, AIBN, benzene, reflux, 3 h	**I** (87)	76, 373
	Bu_3SnD, AIBN, benzene, reflux, 4 h	 **I** + **II** **I + II** (96), **I**:**II** = 85:15	39

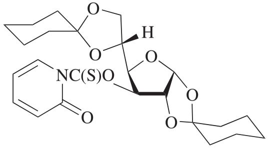
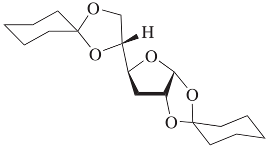
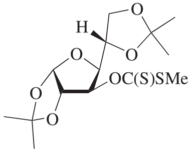
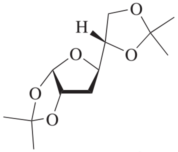
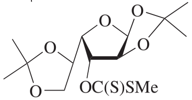
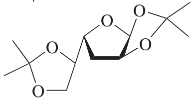
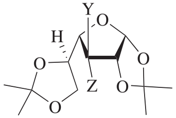
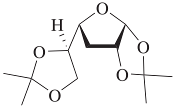
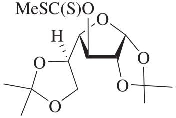
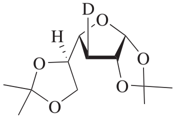
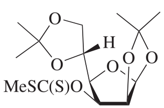
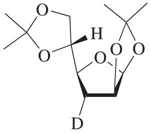
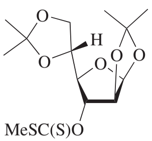
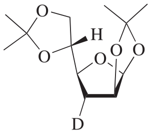
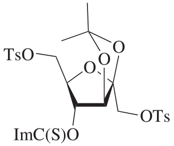
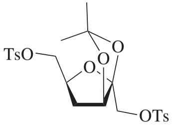
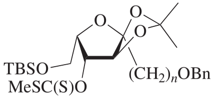
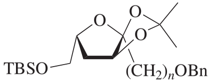
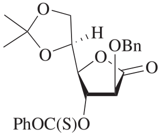
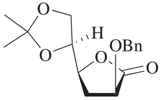
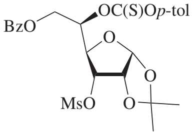
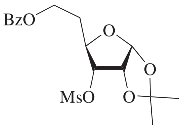
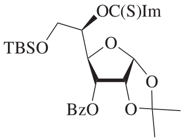
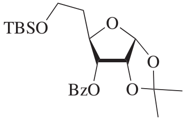
	Bu$_3$SnH, AIBN, toluene, reflux, 1–2 h	 (78)^a	74
	Bu$_3$SnH, toluene, reflux	 (78)^a	460
	Bu$_3$SnH, toluene, reflux, 8 h	 (87)	461
	Bu$_3$SnH, toluene, reflux, 18 h	 Y Z MeSC(S)O H (84) H MeSC(S)O (75)	462
	Bu$_3$SnD, toluene, reflux, 18 h	 (—)	46, 458
	Bu$_3$SnD, toluene, reflux, 3 h	 (44)	47

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Bu_3SnD, toluene, reflux, 3 h	 (57%)	47
	Bu_3SnH, toluene, reflux	 (85)	72
$C_{6–9}$ 	Bu_3SnH, AIBN, toluene, reflux, 16 h	 *n* 1 (81) 4 (100)	463
C_6 	Bu_3SnH, AIBN, toluene, 90°	 (45)[a]	464
	Bu_3SnH, toluene, reflux	 (92)	465
	Bu_3SnH, AIBN, toluene, reflux, 3.75 h	 (87)	452

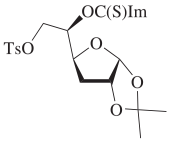
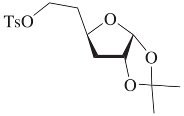
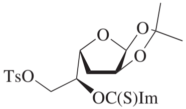
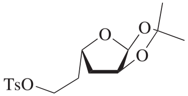
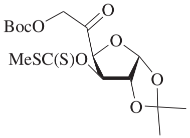
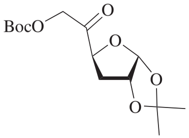
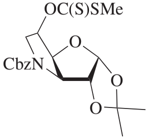
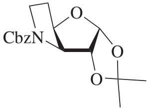
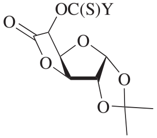
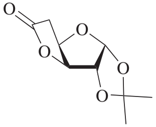
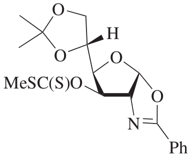
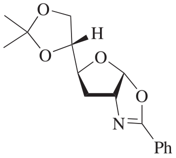
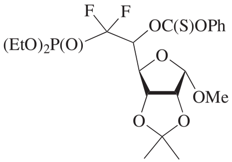
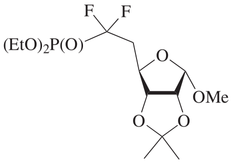
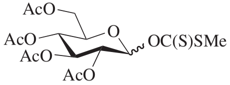
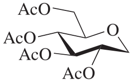
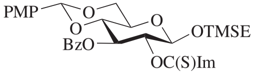
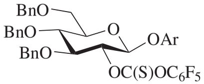
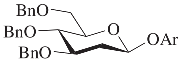
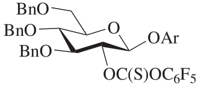
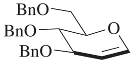
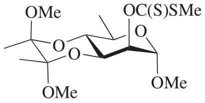
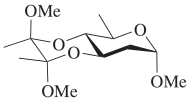
	Bu_3SnH, AIBN, toluene, 80°, 30 min		$(78)^a$	466
	Bu_3SnH, AIBN, toluene, 80°, 1 h		$(85)^a$	466
	Bu_3SnH, toluene, reflux, 16 h		(71)	467
	Bu_3SnH, AIBN, toluene, reflux		(—)	468
	Bu_3SnH, AIBN, solvent		Y Solvent Temp OPh toluene reflux $(94)^a$ SPh — — (81)	 469 470
	Bu_3SnH, AIBN, toluene, 80°, 17 h		$(87)^a$	471

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (89)	472
	$Ph_2SiHSiHPh_2$ (1.1 eq), AIBN (0.3 eq), EtOAc, reflux, 16 h	 (42)	186
	Bu_3SnH, AIBN, toluene, reflux	 (99)	473
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 Ar: Ph (100) 4-$MeOC_6H_4$ (70) 3,4-$Me_2C_6H_3$ (77)	127
	Bu_3SnH, AIBN, toluene, 110°, 1 h	 **I** +  **II** Ar / **I** / **II** 2,6-$Me_2C_6H_3$ (40) (—) 2,6-$(MeO)_2C_6H_3$ (10) (—)	127
	Bu_3SnH, AIBN, toluene, reflux	 (73)	474

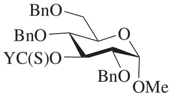
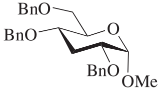
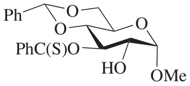
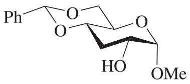
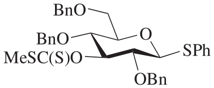
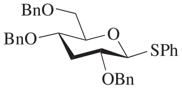
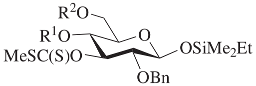
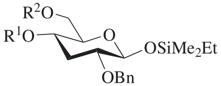
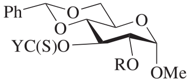
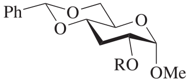
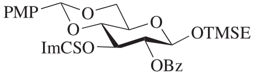
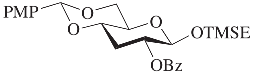
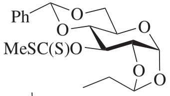
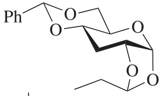
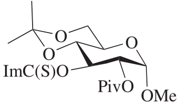
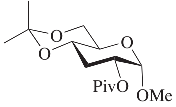
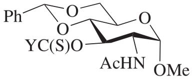
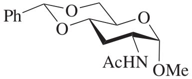
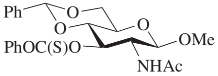
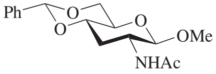
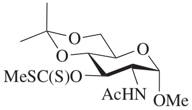
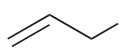
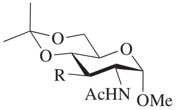
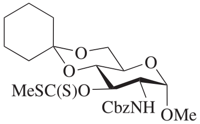
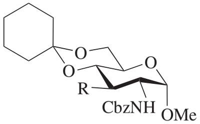
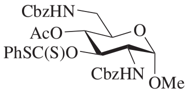
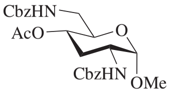
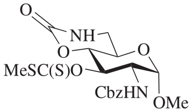
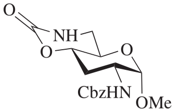
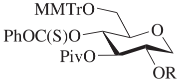
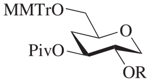
	Bu_3SnH, AIBN, toluene, reflux	 Y · Time (h) MeS · 30 · (95) MeS · 36 · (87)[a] Im · — · (67)	475, 476 477 72
	Bu_3SnH, toluene, reflux, 2.5 h	 (70)	1
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (70)	478
	Bu_3SnH, AIBN, toluene, reflux	 (67)[a]	479
	Bu_3SnH, AIBN, toluene, reflux	 R^1 · R^2 PhCH · (98) H · Bn · (70)	480
	Bu_3SnH, toluene, reflux	 Y · R Im · Ts · (68) 4-MeC_6H_4O · H · (72)	 72 481
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (99)	473
	Bu_3SnH, AIBN, toluene, reflux, 16 h	 (95)	482
	NaH_2PO_2 (10 eq), AIBN (1.5 eq), 2-ME, 105°, 0.5 h	 (87)[a]	483

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)		Refs.
C_6				
	Bu_3SnH, toluene, reflux		Y Im (91) MeS (68)	 484, 72 485
	Bu_3SnH, AIBN, toluene, 80°, 2 h		(96)	486
	 SnBu$_3$, AIBN, toluene		R H (30) MeSC(O)S (15) CH_2=$CHCH_2$ (45)	487
	*i*-PrOH, $(n\text{-}C_{11}H_{23}CO_2)_2$, collidine, reflux		R H (75) MeSC(O)S (15)	32
	Bu_3SnH, toluene, reflux, 1.5 h		(77)	61
	Bu_3SnH, toluene, reflux, 5 h		(79)	61
	Bu_3SnH, AIBN, toluene, reflux		R H (41)[a] Piv (64)[a]	488

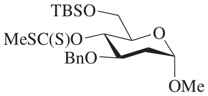
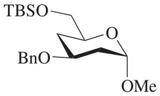
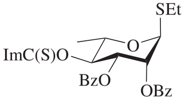
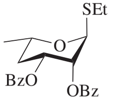
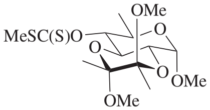
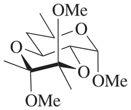
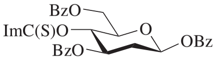
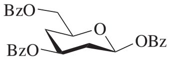
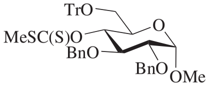
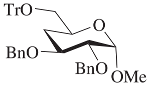
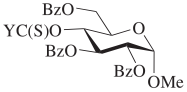
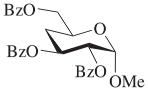
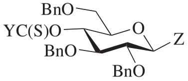
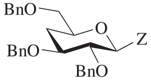
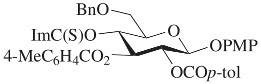
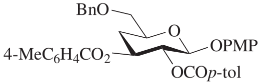
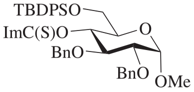
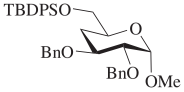
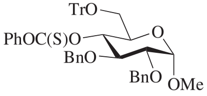
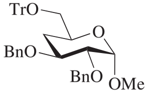
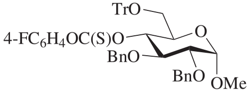
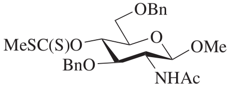
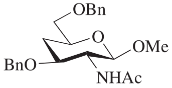
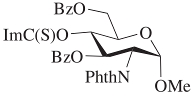
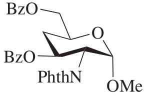
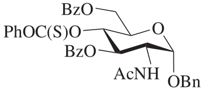
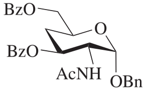
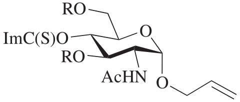
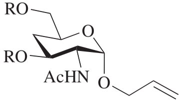
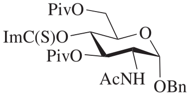
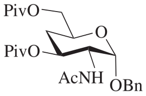
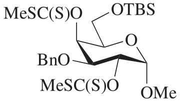
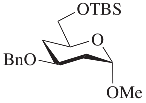
	Bu_3SnH, AIBN, toluene, reflux, 6 h		(79)	489
	Bu_3SnH, toluene, reflux, 1.5 h		(86)^a	490
	Bu_3SnH, AIBN, toluene, reflux		(71)	474
	Bu_3SnH, AIBN, benzene, reflux, 2 h		(76)	491
	Bu_3SnH, AIBN, toluene, reflux, 10 h		(84)^a	492
	Bu_3SnH, AIBN, toluene, reflux		Y MeS (80) PhO (94)	493 494
	Bu_3SnH, AIBN, toluene, reflux		Y Z Time (h) PhO SPh 1 (82)^a MeS OMe 18 (98)	495 496
	Bu_3SnH, AIBN, toluene		(95)	497
	Bu_3SnH, toluene, reflux, 16 h		(77)^a	498

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	Bu_3SnH, AIBN, toluene, 80°, 0.75 h	 **I** (95)	499
	H_3PO_2, Et_3N, AIBN, dioxane, reflux, 3 h	**I** (84)	499
	Bu_3SnH, AIBN, toluene, reflux, 20 min	 (70)	500
	Bu_3SnH, AIBN, toluene, reflux, 18 h	 (87)	501
	Bu_3SnH, AIBN, toluene, 0.5 h	 (95)	502
	Bu_3SnH, AIBN, toluene, reflux	 R Time (h) Bz — (91) Piv 17 (94)	503 504
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (86)	374
	Bu_3SnH, AIBN, reflux, 36 h	 (34)^b	505

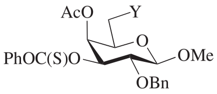
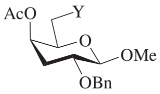
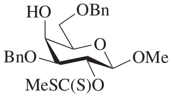
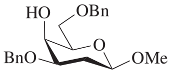
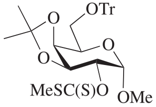
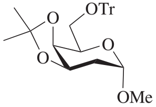
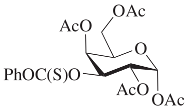
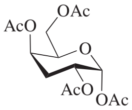
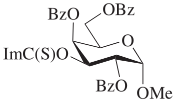
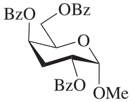
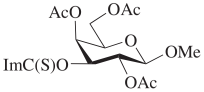
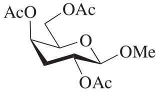
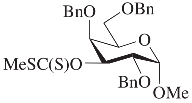
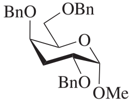
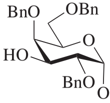
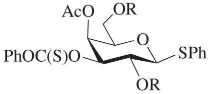
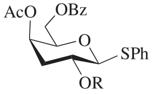
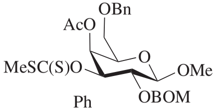
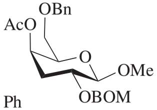
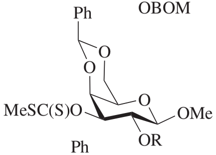
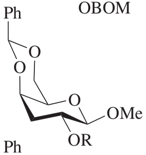
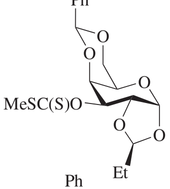
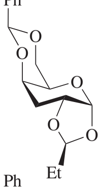
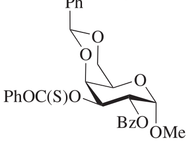
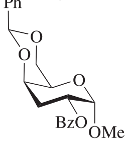
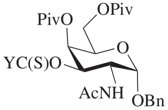
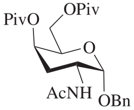
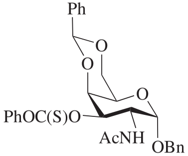
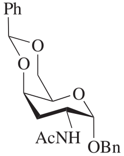
	Bu$_3$SnH, AIBN, toluene, 70°, 5 h	 Y OBn (71) H (82)	506
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h	 (96)	507
	Bu$_3$SnH, toluene, reflux, 2.5 h	 (88)^a	508
	Bu$_3$SnH, AIBN, toluene, 80°, 1 h	 (82)	149
	Bu$_3$SnH, toluene, reflux	 (92)	72
	Bu$_3$SnH, AIBN, toluene, reflux, 30 h	 (72)	476
	Bu$_3$SnH, AIBN, toluene, reflux, 30 h	 (42) +  (31)	476
	Bu$_3$SnH, AIBN, solvent	 R Solvent Temp (°) Time (h) Bz toluene 60 3 (75) Bn benzene 80 2 (64)^a	509 495

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		Bu_3SnH, toluene, reflux, 17 h	 (64)	510
		Bu_3SnH, toluene, reflux, 17 h	 R / BOM (71) Ac (79)	510
		Bu_3SnH, AIBN, toluene, reflux, 5 h	 (98)	482
		Bu_3SnH, toluene, reflux, 15 h	 (96)[a]	494
		Bu_3SnH, AIBN, toluene, reflux, 4 h	 Y / Im (82) PhO (80)	374
		Bu_3SnH, AIBN, toluene, 80°, 2 h	 (79)	502

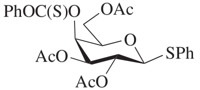
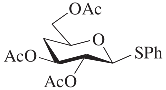
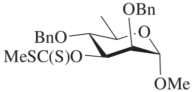
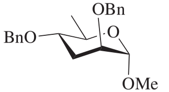
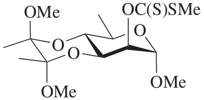
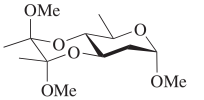
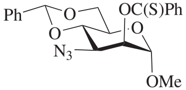
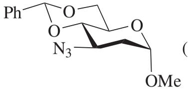
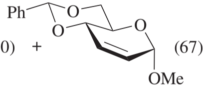
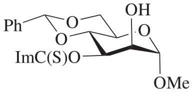
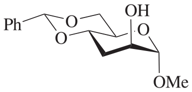
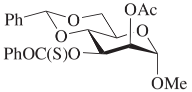
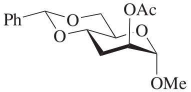
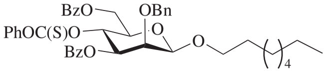
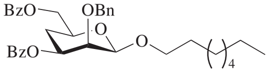
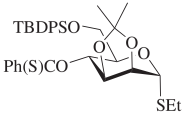
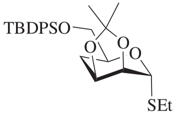
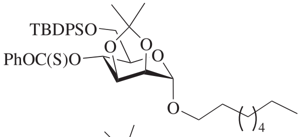
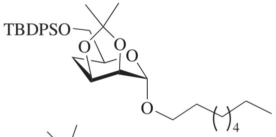
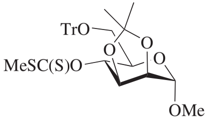
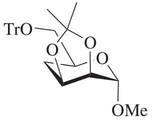
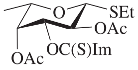
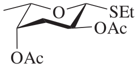
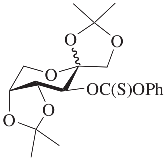
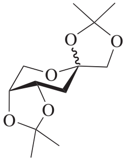
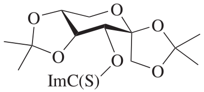
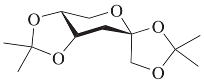
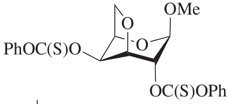
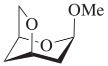
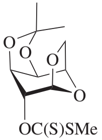
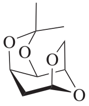
	Bu_3SnH, AIBN, toluene, 60°, 3 h	 (73)	509
	Bu_3SnH, AIBN, toluene, 110°, 2 h	 (48)	511
	Bu_3SnH, AIBN, toluene, heat	 (73)	474
	Bu_3SnH, AIBN, benzene, reflux, 1 h	 (20) +  (67)	125
	$(TMS)_3SiH$, AIBN, toluene, reflux, 40 min	 (68)	512
	Bu_3SnH, AIBN, toluene, 90°, 40 min	 (77)	513
	Bu_3SnH, AIBN, toluene, 0.5 h	 (83)	514
	Bu_3SnH, AIBN, benzene, reflux, 10 min	 (58)^b	515

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (88)	516
	H_3PO_2, AIBN, Et_3N, dioxane, reflux	 (90)	517
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (92)	93
	$(TMS)_3SiH$, AIBN, benzene, reflux, 3 h	 (97)	518
	Bu_3SnH, toluene, reflux	 (65)	72
	Bu_3SnH, AIBN, toluene, reflux	 (46)	519
	Bu_3SnH, toluene, reflux, 16 h	 (94)[a]	1

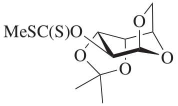
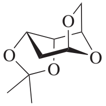
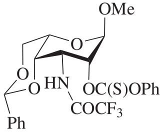
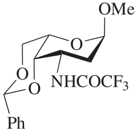
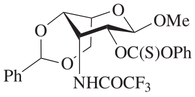
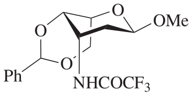
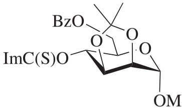
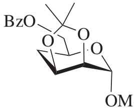
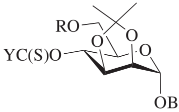
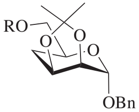
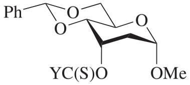
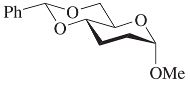
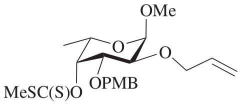
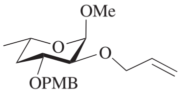
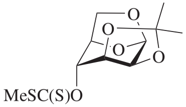
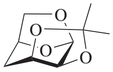
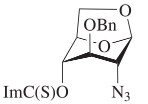
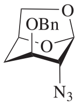
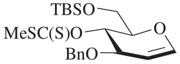
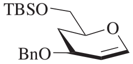
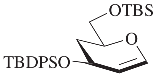
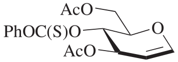
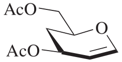
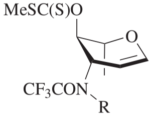
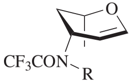
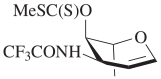
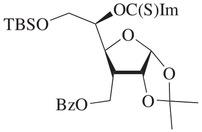
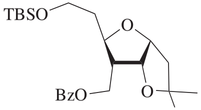
	Bu_3SnH, toluene, reflux, 16 h	 (89)[a]	1
	Bu_3SnH, AIBN, toluene, 60°, 1.5 h	 (80)	520
	Bu_3SnH, AIBN, toluene, 60°, 1.5 h	 (80)	521
	Bu_3SnH, toluene, reflux	 (87)	522, 72
	Bu_3SnH, AIBN, toluene	 Y R Temp (°) Im Bz reflux (87) MeS TBDPS 80 (84)	523
	Bu_3SnH, toluene, reflux	 Y H (29) MeS (90)	28 524
	Bu_3SnH, AIBN, benzene, reflux, 20 min	 (73)	332
	Bu_3SnH, toluene, reflux, 24 h	 (88)	525

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	Bu_3SnH, AIBN, benzene, reflux, 1.5 h	 (55)	121
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 (73)	275, 526
	Bu_3SnH, AIBN, toluene, reflux	 (85)	276
	Bu_3SnH, AIBN, toluene, reflux	 (72)[a]	527
	Bu_3SnH, AIBN, toluene	 R H (68) Me (>90)	528
	Bu_3SnH, AIBN, toluene	 (70)	528
C_7			
	Bu_3SnH, AIBN, toluene, reflux	 (65)	529

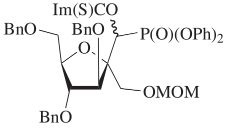
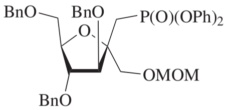
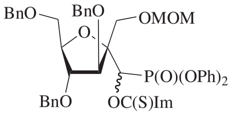
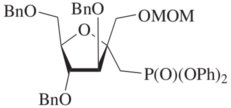
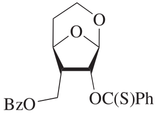
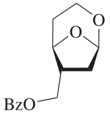
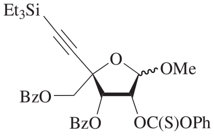
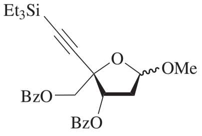
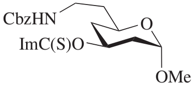
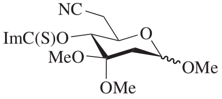
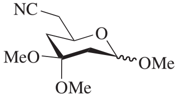
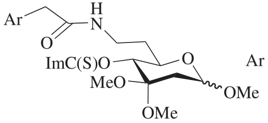
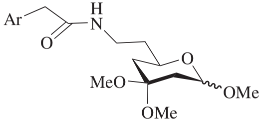
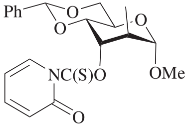
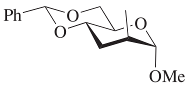
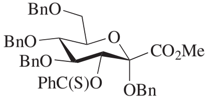
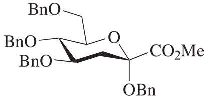
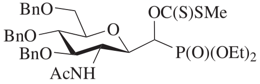
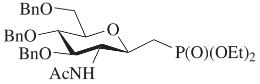
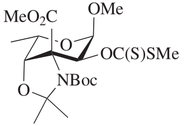
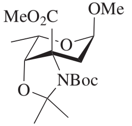
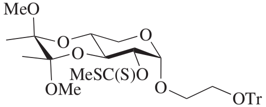
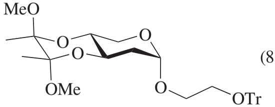
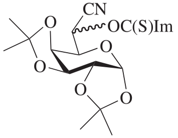
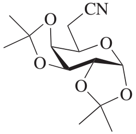
	Bu_3SnH, toluene, ia, reflux, 4 h	 (79)	530
	Bu_3SnH, toluene, ia, reflux, 2 h	 (77)	530
	Bu_3SnH, AIBN	 (—)	529
	Bu_3SnH, AIBN, toluene, 85°, 2 h	 (70)	530a
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 (61)[a]	531
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (29)	532
	Bu_3SnH, AIBN, toluene, reflux, 7 h	 (89)	533

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7  Ar = 3,4-$Cl_2C_6H_3$	$(TMS)_3SiH$, AIBN, toluene, reflux, 21 h	 (90)	533
	Bu_3SnH, AIBN, toluene, reflux, 1–2 h	 (80)[a]	74
	Bu_3SnH, AIBN, toluene, 90°, 2 h	 (64)	534
	Bu_3SnH, AIBN, toluene, 80°, 20 min	 (46)[a]	535
	Bu_3SnH, AIBN, benzene, reflux, 4 h	 (95)	536
	Bu_3SnH, AIBN, toluene, reflux	 (86)	537
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 30 min	 (85)[b]	27

C$_8$

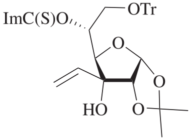
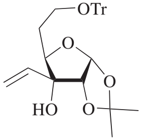
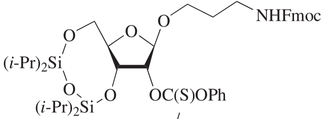
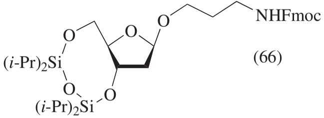
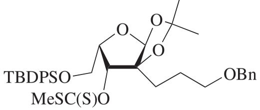
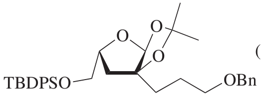
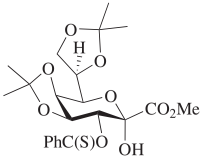
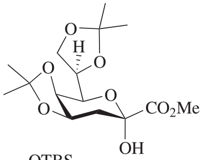
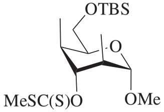
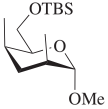
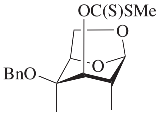
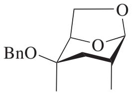
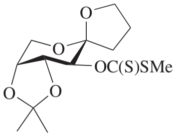
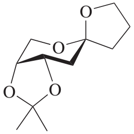
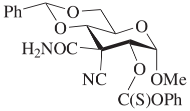
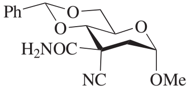
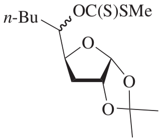
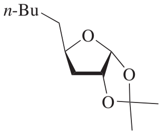
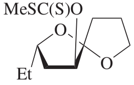
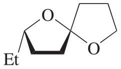
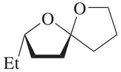
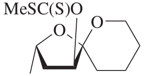
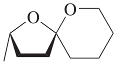
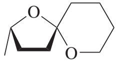
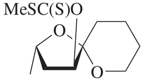
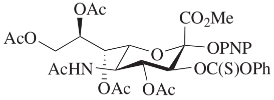
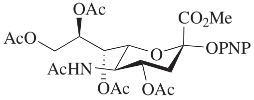
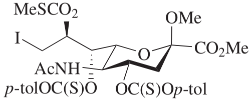
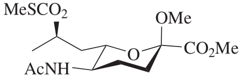
	Bu_3SnH, AIBN, toluene, reflux	 (75)	538
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (66)	539
	Bu_3SnH, AIBN, toluene, reflux, 15 h	 (86)	540
	Bu_3SnH, AIBN, toluene, 90°, 2 h	 (83)	541
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 (80)	531
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (86)	542
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (89)	543

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	Bu_3SnH, AIBN, benzene, reflux, 4 h	 (85)	536
C_9			
	Bu_3SnH, AIBN, toluene, reflux, 10 h	 (81)	544
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 **I** +  **II** **I** + **II** (22), **I**:**II** (—)	540
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 **I** +  **II** **I** + **II** (74), **I**:**II** (—)	463
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	**I** + **II** (80), **I**:**II** (—)	463
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (92)	119
	Bu_3SnH, toluene, reflux, 2.5 h	 (83)	113

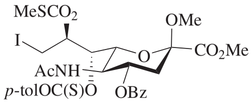
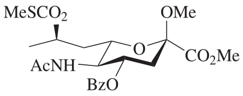
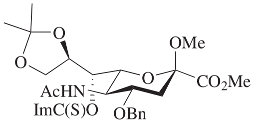
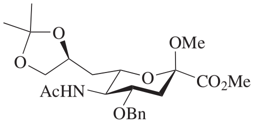
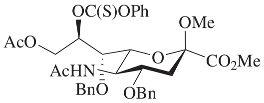
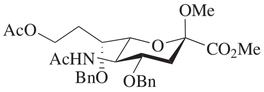
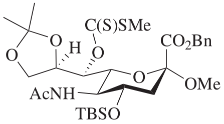
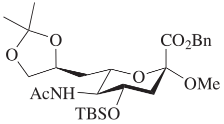
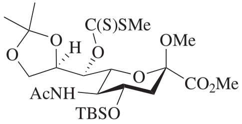
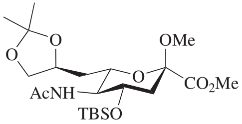
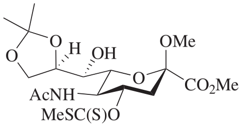
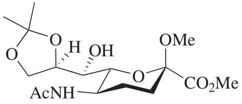
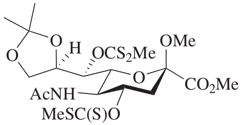
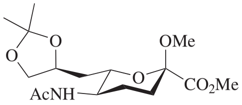
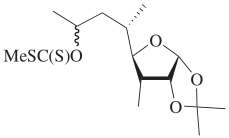
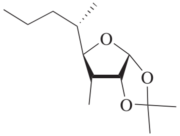
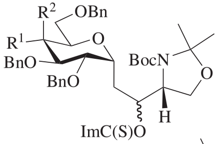
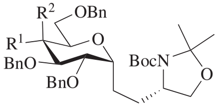
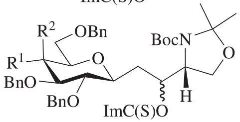
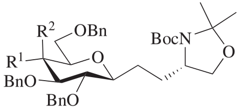
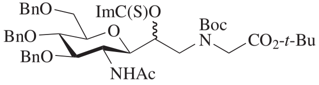
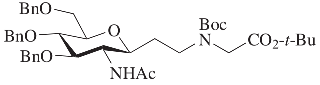
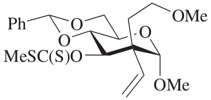
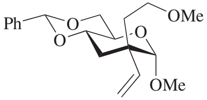
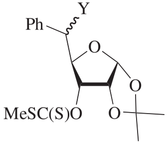
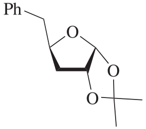
	Bu_3SnH, toluene, reflux, 2.5 h		(86)	113
	Bu_3SnH, AIBN, toluene, 80°, 0.5 h		(80)[a]	384
	Bu_3SnH, AIBN, toluene, 100°, 0.5 h		(68)[a]	384
	Bu_3SnH, xylenes, heat		(—)	545
	Bu_3SnH, xylene, 120°, 2.5 h		(—)	380
	Bu_3SnH, xylene, 120°, 2.5 h		(—)	380
	Bu_3SnH, xylene, 120°, 2.5 h		(—)	380

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (73)	546
	Bu_3SnH, AIBN, toluene, 85°, 2 h	 R^1 R^2 BnO H $(60)^b$ H BnO $(60)^b$	 547 548
	Bu_3SnH, AIBN, toluene, 85°, 2 h	 R^1 R^2 BnO H $(55)^b$ H BnO $(60)^b$	 547 548
	Bu_3SnH, AIBN	 $(67)^a$	549
	Bu_3SnH, toluene, reflux	 (—)	550
C_{11} 	Bu_3SnH, AIBN, toluene, reflux, 6 h	 Y H (74) MeSCSO (77)	551

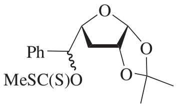
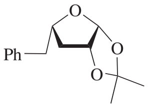
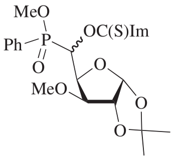
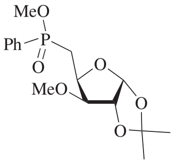
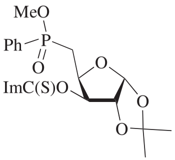
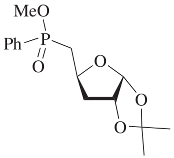
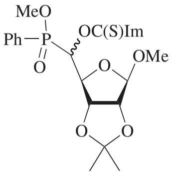
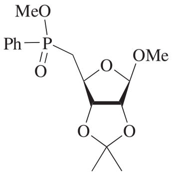
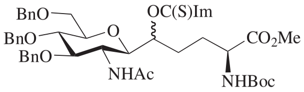
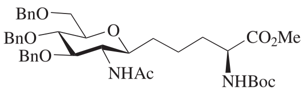
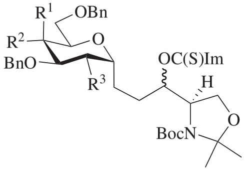
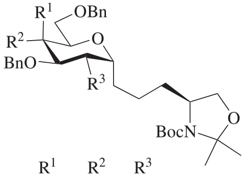
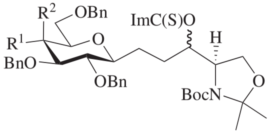
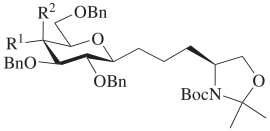
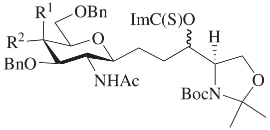
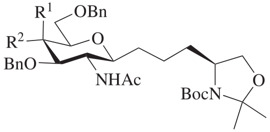
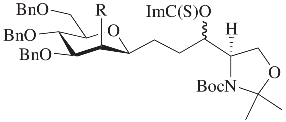
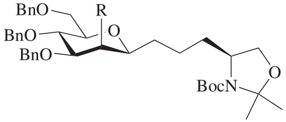
C_{11}		Bu_3SnH, AIBN, toluene, reflux, 6 h	 (79)	552
		Bu_3SnH, toluene, reflux, 1.5 h	 (99)	552, 553
		Bu_3SnH, AIBN	 (—)	416
		Bu_3SnH, AIBN, toluene, reflux	 (—)	554, 555, 436
		Bu_3SnH, AIBN	 (67)^b	556

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	Bu_3SnH, AIBN, toluene, 85°, 2 h	 R¹ R² R³ BnO H BnO (62)[b] BnO H AcNH (51)[b] H BnO BnO (69)[b] H BnO AcNH (76)[b]	557
	Bu_3SnH, AIBN, toluene, 85°, 2 h	 R¹ R² BnO H (50)[b] H BnO (50)[b]	 558, 548 557
	Bu_3SnH, AIBN, toluene, 85°, 2 h	 R¹ R² H BnO (66)[b] BnO H (89)[b]	557
	Bu_3SnH, AIBN, toluene, 85°, 2 h	 R BnO (74)[b] AcNH (77)[b]	557

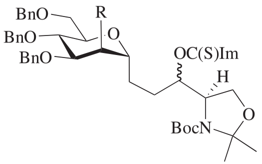
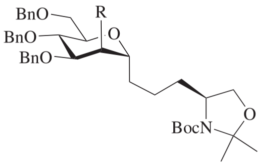
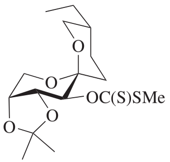
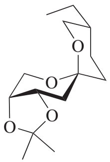
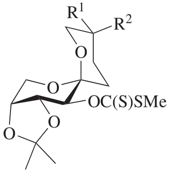
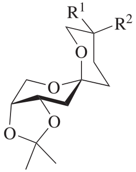
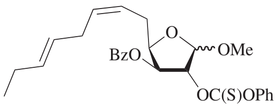
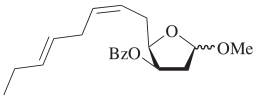
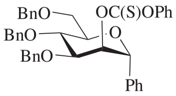
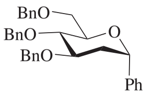
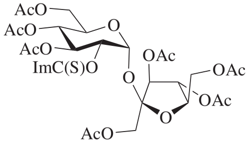
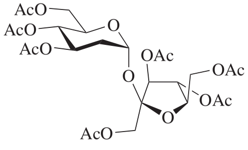
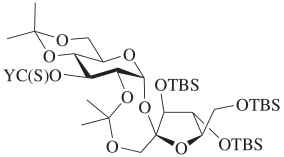
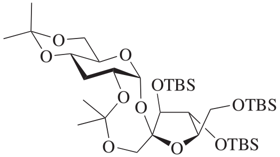
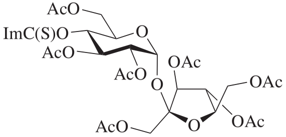
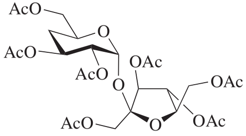
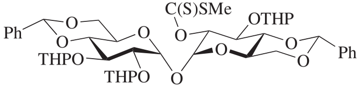
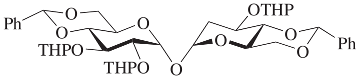
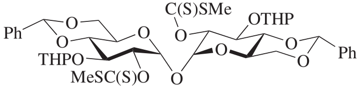
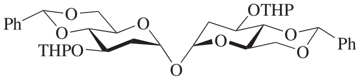
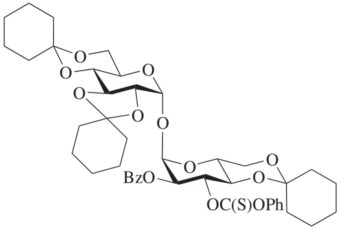
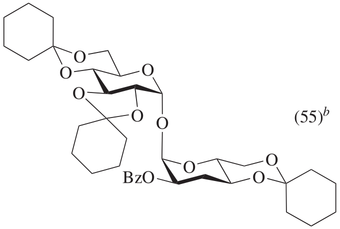
		Bu$_3$SnH, AIBN, toluene, 85°, 2 h		R BnO (74)^b AcNH (71)^b	557
		Bu$_3$SnH, AIBN, toluene, reflux, 15 h		(84)	559
		H$_3$PO$_2$, AIBN, Et$_3$N, dioxane–H$_2$O, reflux, 1.5–2 h		R^1 R^2 Et H (95) H Et (92)	198
C$_{12}$		Bu$_3$SnH, AIBN, toluene, reflux, 2 h		(78)	560
		Bu$_3$SnH, AIBN, toluene, 100°, 1 h		(84)	561
		Bu$_3$SnH, toluene, reflux, 3 h		(81)	562

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Bu_3SnH, toluene, reflux, 3 h	 Y Im (76) MeS (93)[a]	 274 273
	Bu_3SnH, toluene, reflux, 9 h	 (83)	274
	Bu_3SnH, toluene, reflux	 (90)	563
	Bu_3SnH, toluene, reflux	 (84)	563
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (55)[b]	393

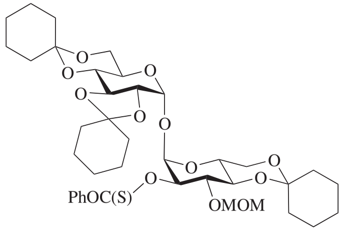
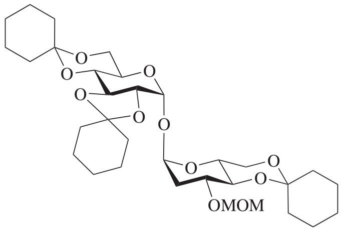
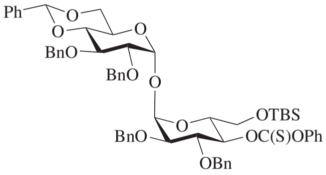
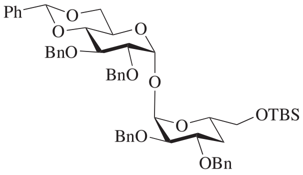
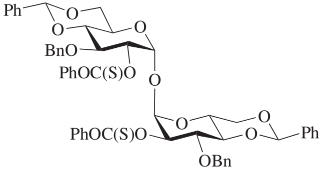
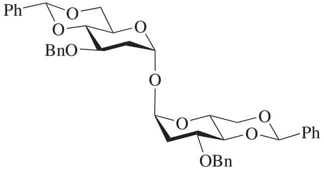
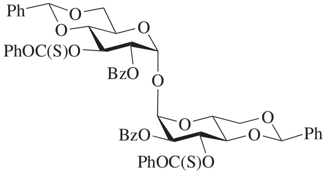
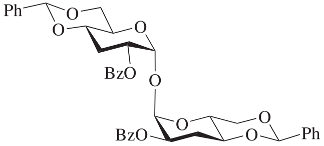
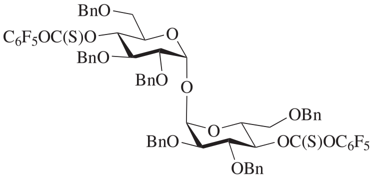
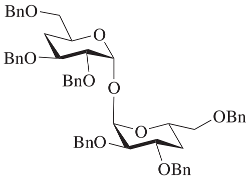
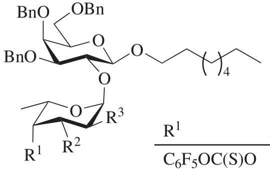
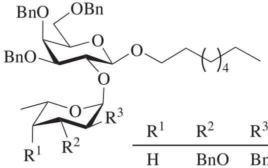
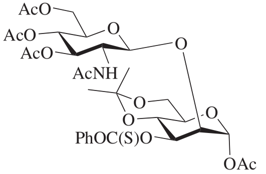
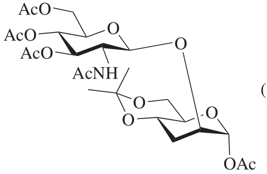
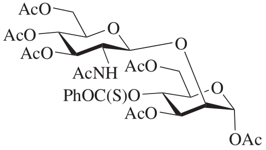
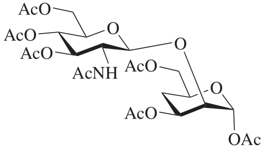
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h		(40)^b	393
	Bu$_3$SnH, AIBN, toluene, reflux, 0.25 h		(58)^b	393
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h		(51)^b	393
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h		(67)^a	393

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (36)[b]	393
 R^1 / R^2 / R^3 $C_6F_5OC(S)O$ / BnO / BnO BnO / $C_6F_5OC(S)O$ / BnO BnO / BnO / $C_6F_5OC(S)O$	Bu_3SnH, AIBN, toluene, reflux, 4 h	 R^1 / R^2 / R^3 H / BnO / BnO (66) BnO / H / BnO (76) BnO / BnO / H (61)	564
	Bu_3SnH, AIBN, dioxane, 90°, 1 h	 (91)	565
	Bu_3SnH, AIBN, dioxane, reflux, 0.5 h	 (67)	514

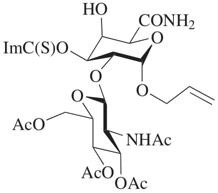
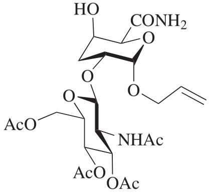
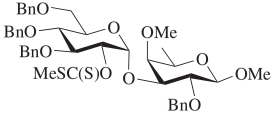
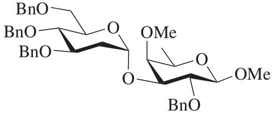
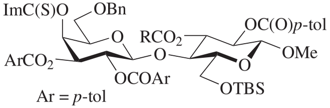
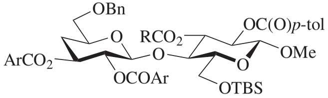
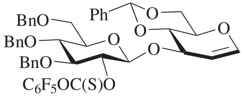
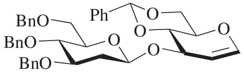
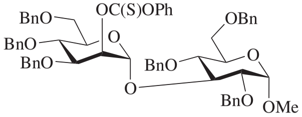
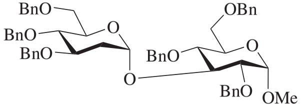
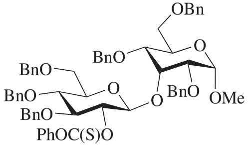
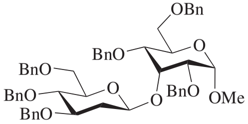
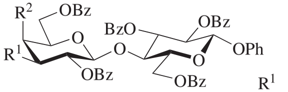
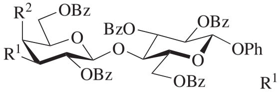
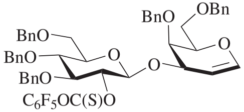
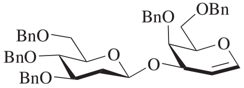
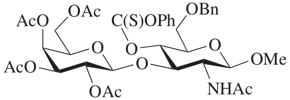
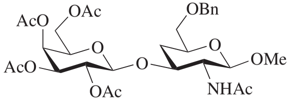
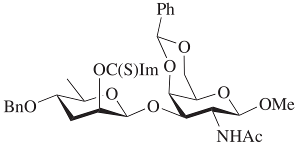
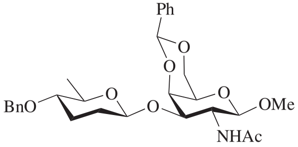
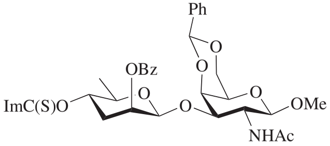
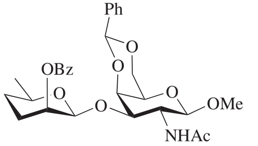
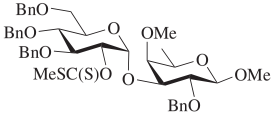
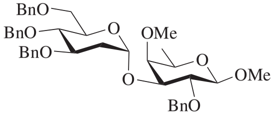
	Bu$_3$SnH, toluene, reflux	 (71)	566
	Bu$_3$SnH, AIBN, toluene, reflux, 3 h	 (82)^b	567
 Ar = *p*-tol	Bu$_3$SnH, AIBN, toluene, reflux	 (80)	497
	Bu$_3$SnH, AIBN, toluene, reflux, 1 h	 (62)	127
	Bu$_3$SnH, AIBN, toluene, reflux, 3 h	 (72)	568
	Bu$_3$SnH, AIBN, toluene, reflux, 3 h	 (75)	568

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}  R^1 / R^2 HO / PhOC(S)O PhOC(S)O / HO	Bu_3SnH, AIBN, benzene, reflux, 1 h	 R^1 / R^2 HO / H (8)[a] H / HO (76)[a]	569
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (83)	127
	Bu_3SnH, AIBN, toluene, 80°, 2 h	 (74)	486
	Bu_3SnH, AIBN, toluene, reflux, 8 h	 (95)	570
	Bu_3SnH, AIBN, toluene, reflux, 8 h	 (92)	570
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (82)[b]	567

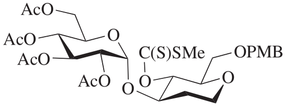
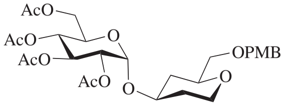
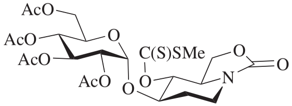
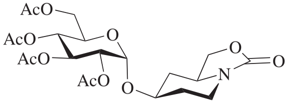
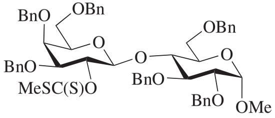
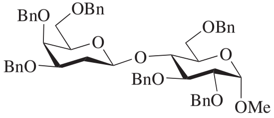
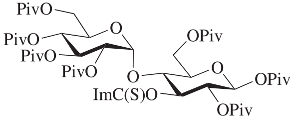
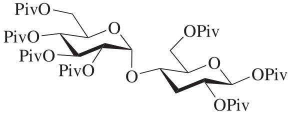
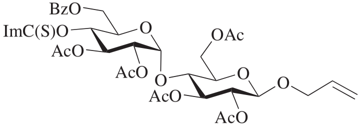
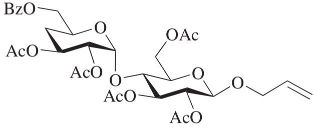
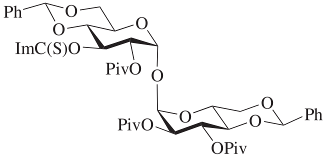
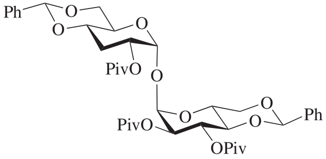
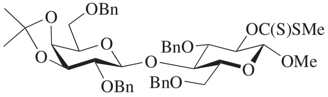
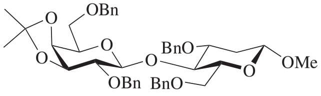
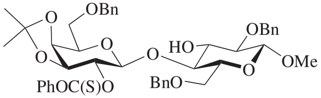
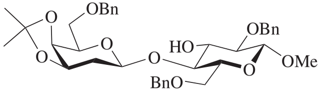
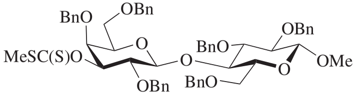
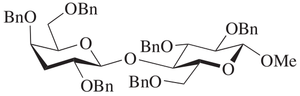
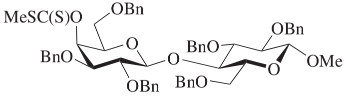
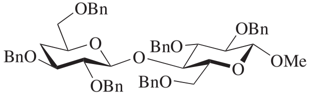
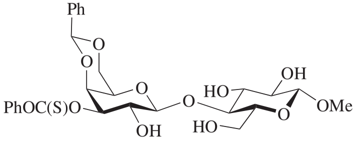
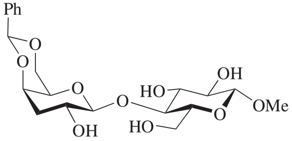
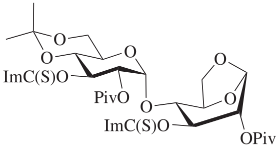
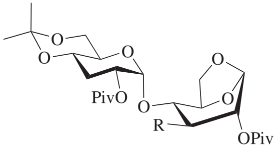
	Bu_3SnH, toluene, reflux, 4 h		(73)[a]	571
	Bu_3SnH, toluene, reflux, 4 h		(79)[a]	572
	Bu_3SnH, AIBN, toluene, reflux, 3 h		(77)[b]	567, 573
	Bu_3SnH, AIBN, toluene, reflux, 1 h		(94)	574
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h		(92)	575
	Bu_3SnH, AIBN, toluene, reflux, 16 h		(83)	576

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (73)[b]	577
	Bu_3SnH, AIBN, toluene, reflux, 30 h	 (84)	577
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (77)[a]	577
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (85)[a]	577
	Bu_3SnH, AIBN, toluene, reflux, 10 h	 (68)[b]	577
	Bu_3SnH, AIBN, toluene, reflux, 0.25 h	 R: H (83) OH (15)	576

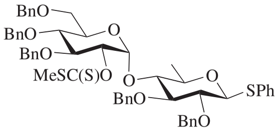
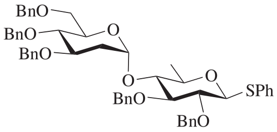
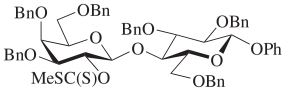
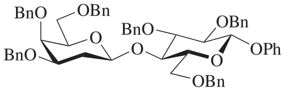
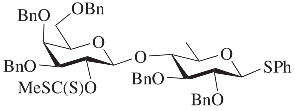
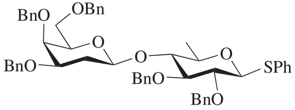
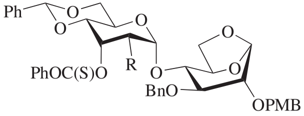
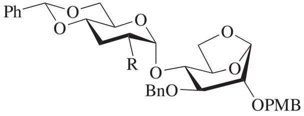
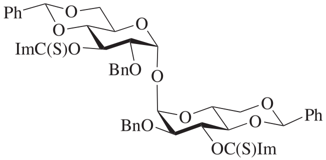
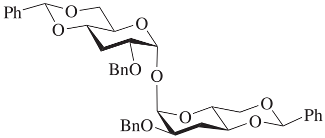
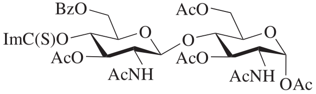
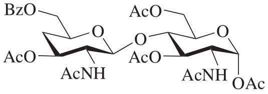
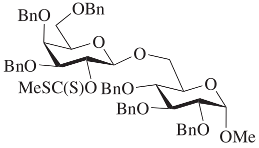
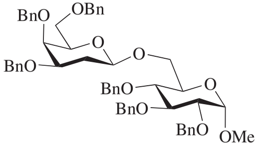
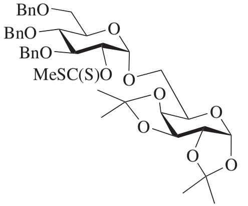
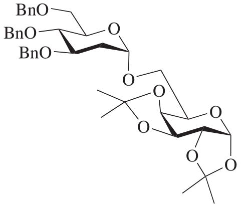
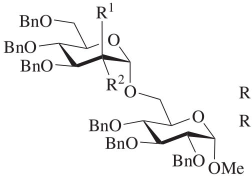
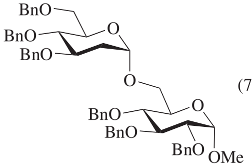
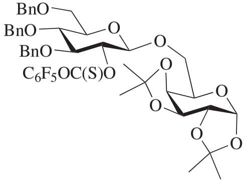
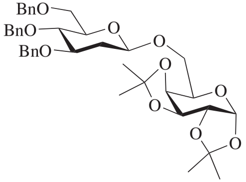
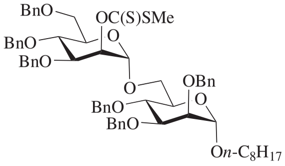
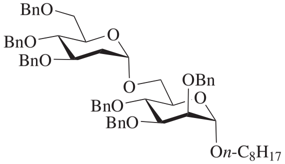
	Bu_3SnH, AIBN, toluene, reflux, 3 h		(82)[b]	567, 573
	Bu_3SnH, AIBN, toluene, 75°, 8 h		(62)[a]	569
	Bu_3SnH, AIBN, toluene, reflux, 3 h		(80)[b]	567
	Bu_3SnH, AIBN, toluene, 80°, 1.5 h		R N_3 (0) NHCbz (96)	124
	Bu_3SnH, AIBN, toluene, reflux, 16 h		(66)	578
	Bu_3SnH, AIBN, toluene, reflux		(72)	579
	Bu_3SnH, AIBN, toluene, reflux, 3 h		(95)[b]	567, 573

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}					
		Bu_3SnH, AIBN, toluene, reflux, 3 h		$(70)^b$	567, 573
	$R^1 = PhOC(S)O$; $R^2 = H$ $R^1 = H$; $R^2 = PhOC(S)O$	Bu_3SnH, AIBN, toluene, reflux, 3 h		(74)	568
		Bu_3SnH, AIBN, toluene, reflux, 1 h		(90)	127
		Bu_3SnH, AIBN, toluene, reflux		(61)	580

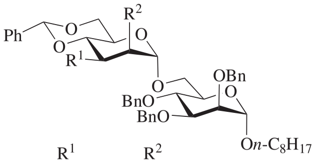
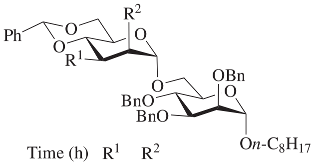
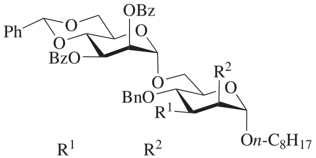
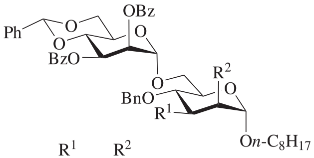
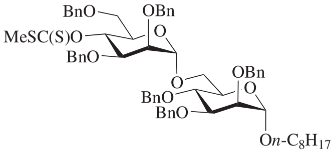
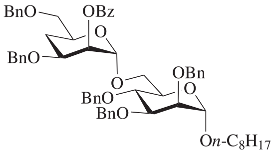
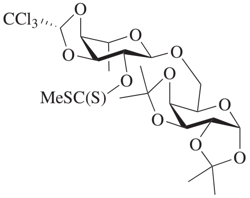
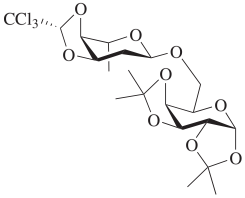
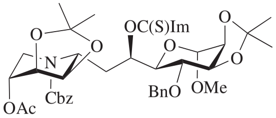
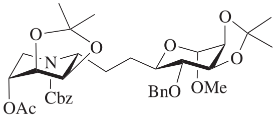
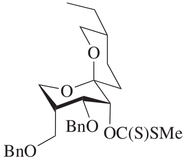
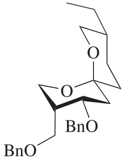
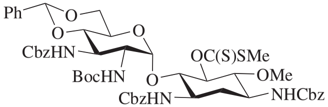
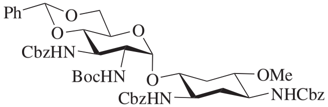
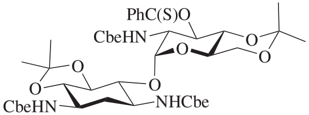
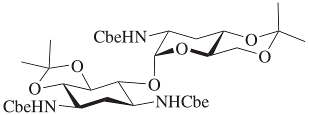
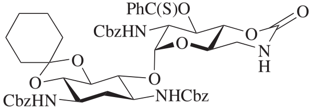
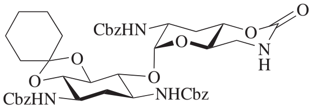
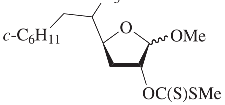
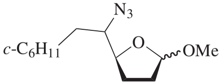
 R¹ R² BnO MeSC(S)O MeSC(S)O BnO	Bu_3SnH, AIBN, toluene, reflux	 Time (h) R¹ R² 3 BnO H (41) 1 H BnO (37)	516
 R¹ R² BzO MeSC(S)O MeSC(S)O BzO	Bu_3SnH, AIBN, toluene, reflux, 3 h	 R¹ R² BzO H (84) H BzO (32)	516
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (64)	516
	Bu_3SnH, AIBN, toluene, reflux, 13 h	 (76)[a]	98

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	Bu_3SnH, AIBN, toluene, reflux	 (48)[b]	581
	Bu_3SnH, AIBN, toluene, reflux, 10 min	 (94)	582
	Bu_3SnH, toluene, reflux, 50 min	 (92)	583
	Bu_3SnH, toluene, reflux	 (51)	584
	Bu_3SnH, toluene, reflux	 (90)	584
C_{12} 	Bu_3SnH, AIBN, toluene, 100°, 10 min	 (61)	120

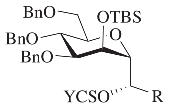
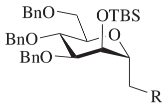
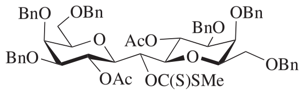
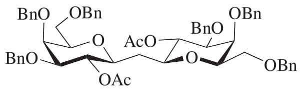
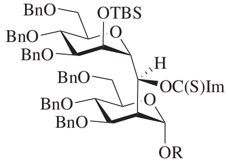
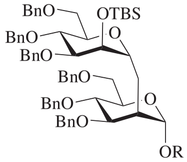
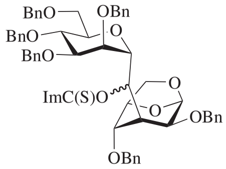
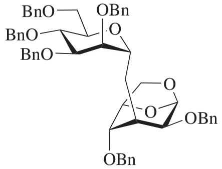
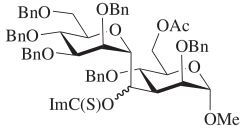
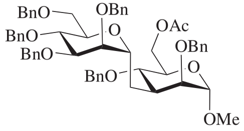
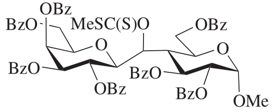
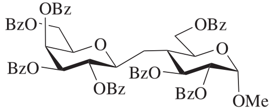
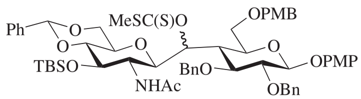
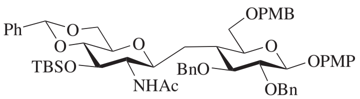
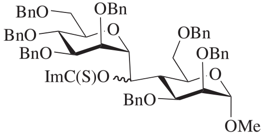
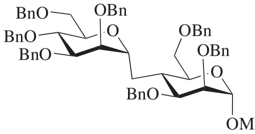
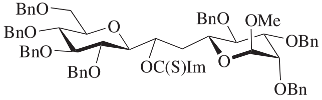
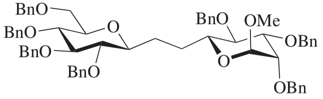
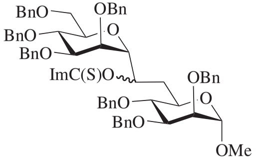
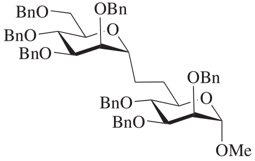
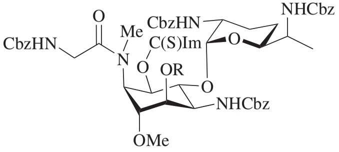
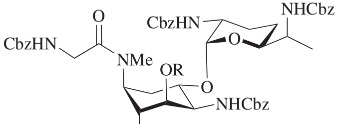
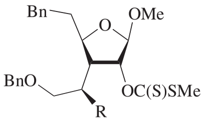
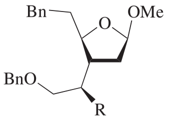
C_{13-14} 	Bu_3SnH, AIBN, toluene, 90°	 Y R C_6F_5 c-C_6H_{11} (70) Im n-C_7H_{15} (69)	585
C_{13} 	Bu_3SnH, AIBN, toluene, reflux, 10 min	 (85)	586
	MH, AIBN, additive, toluene, reflux	 MH R Additive Bu_3SnH Me — (38) Bu_3SnH Me C_6F_5OH (70) Ph_3SnH PMB C_6F_5OH (90)	585
	Ph_3SnH (3 eq), AIBN, C_6F_5OH (2 eq), toluene, reflux, 3 h	 (56)	161
	Ph_3SnH (3 eq), AIBN, C_6F_5OH (2 eq), toluene, reflux, 0.5 h	 (65)	161
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (84)	587

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	Bu_3SnH, AIBN, toluene, reflux	 (91)	588
	Ph_3SnH (3 eq), AIBN, C_6F_5OH (2 eq), toluene, reflux, 3 h	 (54)	589
	Bu_3SnH, AIBN, toluene, 95°, 2 h	 (89)	590
	Ph_3SnH (3 eq), AIBN, C_6F_5OH (2 eq), toluene, reflux, 3 h	 (73)	161
	Bu_3SnH, dioxane, reflux, 2 h	 R Bn (40) $COCH_2NHCbz$ (63)	591
C_{14-15}			
	Bu_3SnH, AIBN, toluene, 100°, 1 h	 R H (58) Me (—)	592

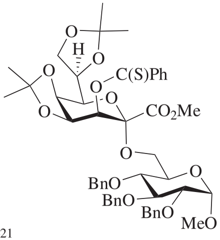
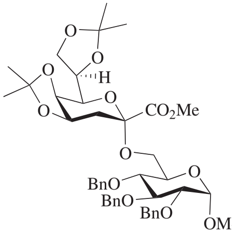
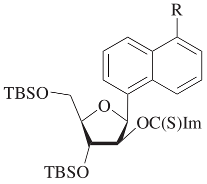
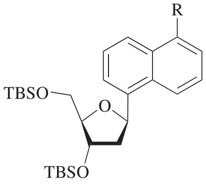
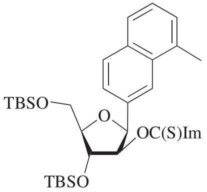
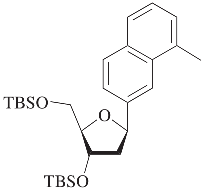
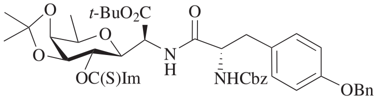
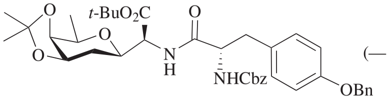
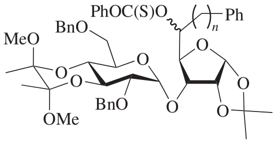
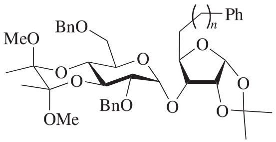
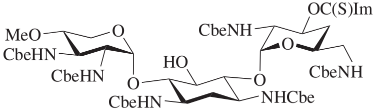
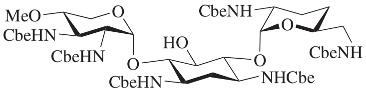
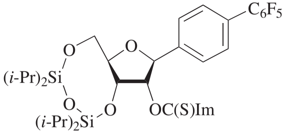
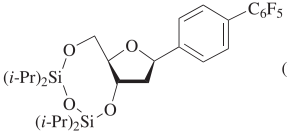
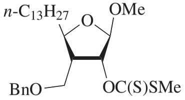
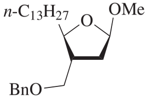
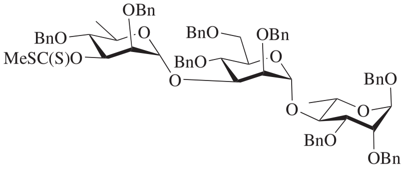
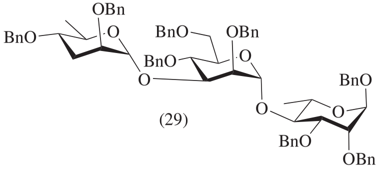
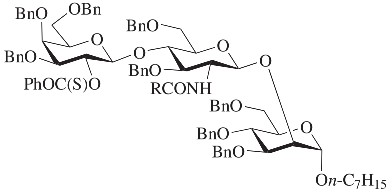
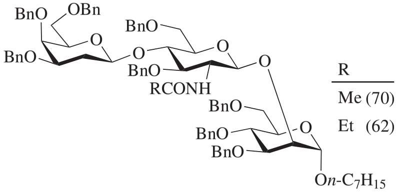
C_{14}		Bu_3SnH, AIBN, toluene, 90°, 2 h		(76)	541
$C_{15–21}$		$(TMS)_3SiH$, AIBN, toluene, reflux		R H (91) Me (68) Ph (86)	593
C_{16}		$(TMS)_3SiH$, AIBN, toluene, reflux		(88)	593
C_{17}		Bu_3SnH, benzene, reflux, 18 h		(—)	594
$C_{17–19}$		Bu_3SnH, AIBN, benzene, reflux		*n* 0 (93) 1 (18) 2 (64)	595

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	Bu_3SnH, toluene, reflux	 (90)	263
	$(TMS)_3SiH$, AIBN, toluene, 85°, 0.5 h	 (79)	596
C_{18}			
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (75)	597
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (29)	511
	Bu_3SnH, AIBN, toluene, 100°, 2 h	 R Me (70) Et (62)	598

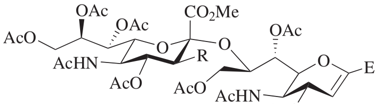
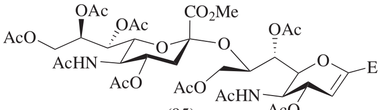
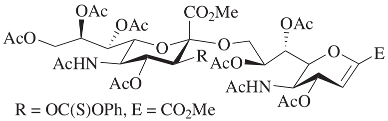
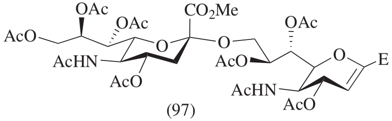
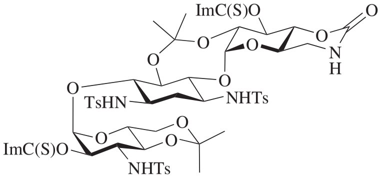
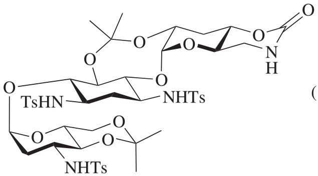
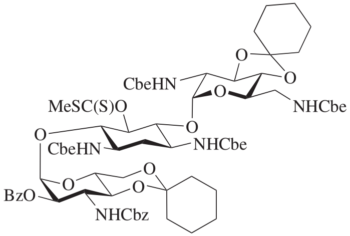
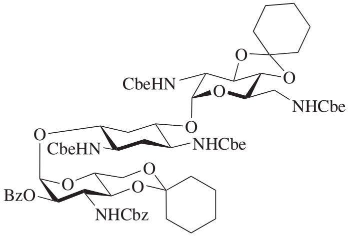
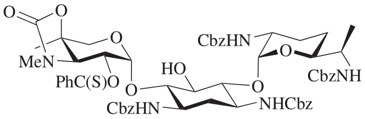
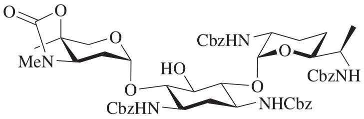
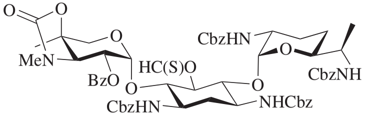
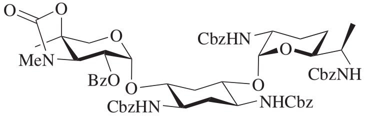
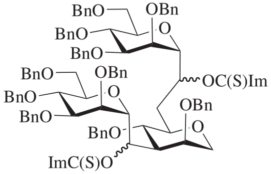
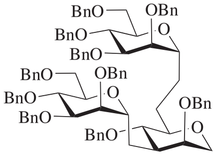
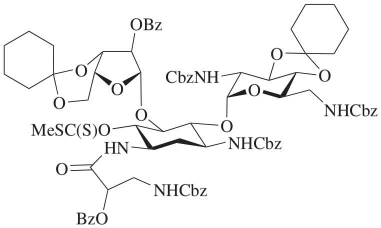
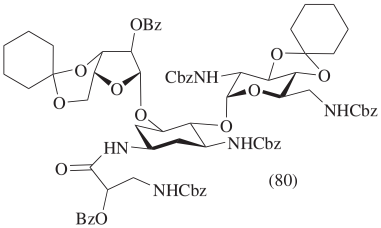
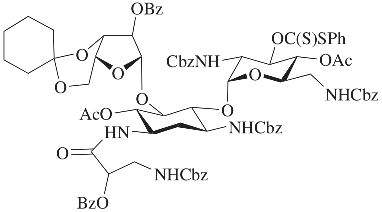
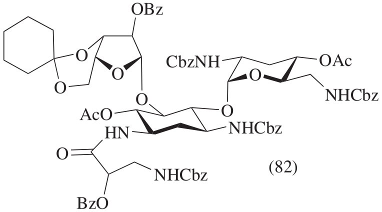
 R = OC(S)OPh, E = CO_2Me	Bu_3SnH, AIBN, toluene, reflux	 (95)		599
 R = OC(S)OPh, E = CO_2Me	Bu_3SnH, AIBN, toluene, reflux, 10 min	 (97)		599
	Bu_3SnH, THF, sealed tube, 110°, 3 h		(86)	600
	Bu_3SnH		(78)	61
C_{19}				
	Bu_3SnH, toluene, reflux		(72)	584

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	Bu_3SnH, toluene, reflux	 (78)	264
C_{20}			
	Ph_3SnH (5 eq), AIBN, C_6F_5OH (4 eq), toluene, reflux, 2.5 h	 (53)	161
	Bu_3SnH, toluene, reflux	 (80)	61
	Bu_3SnH, toluene, reflux	 (82)	61

C$_{21}$

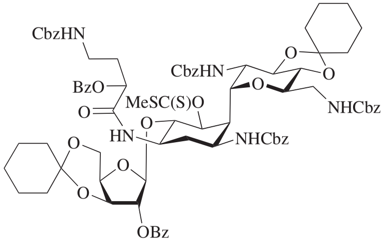
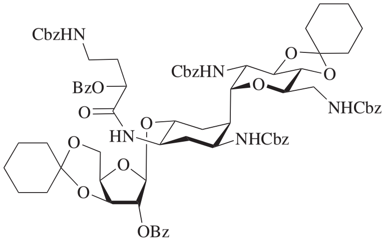
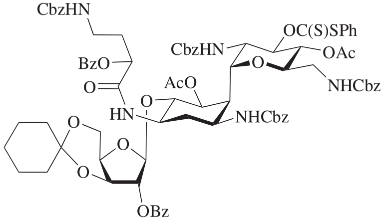
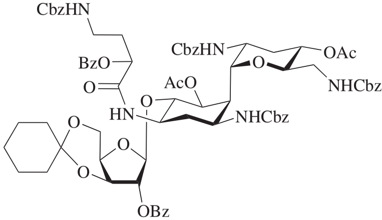
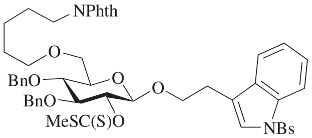
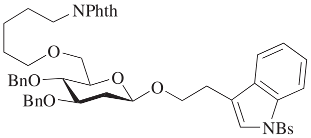
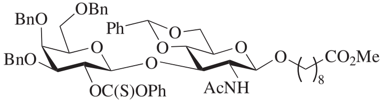
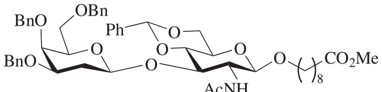
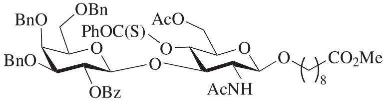
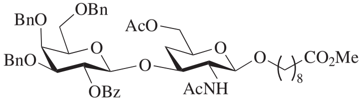
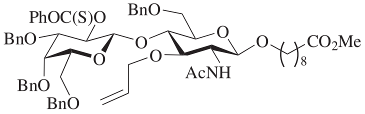
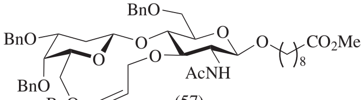
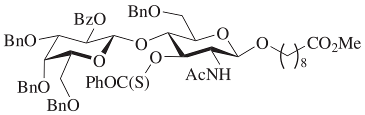
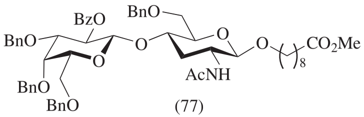
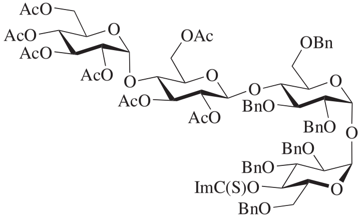
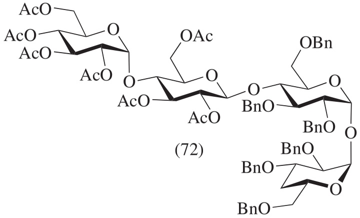
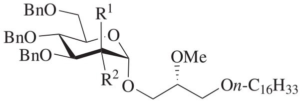
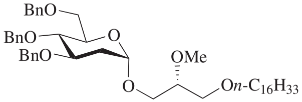
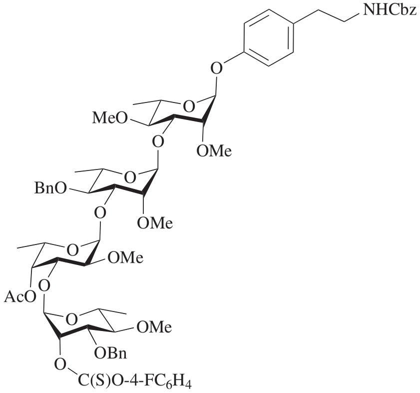
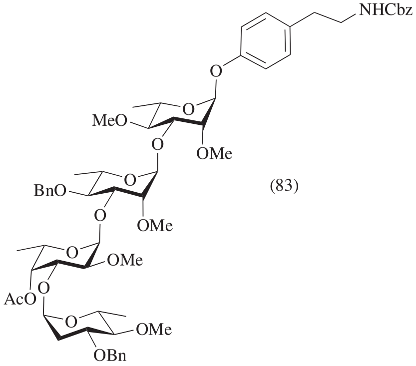
	Bu$_3$SnH, toluene, reflux, 5 h	 (80)	61
	Bu$_3$SnH, toluene, reflux, 3 h	 (82)	61
	Bu$_3$SnH, AIBN, toluene, reflux	 (49)	493
	Bu$_3$SnH, AIBN, toluene, 80°, 2 h	 (64)	486
	Bu$_3$SnH, AIBN, toluene, 80°, 2 h	 (61)	486

TABLE 2A. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	Bu_3SnH, AIBN, toluene, 80°, 2 h	 (57)	486
	Bu_3SnH, AIBN, toluene, 80°, 2 h	 (77)	486
C_{24}			
	Bu_3SnH, AIBN, toluene, reflux, 2.5 h	 (72)	575
C_{25}			
	Bu_3SnH, AIBN, toluene, reflux		601

R^1	R^2	
H	OC(S)SMe	(92)
OC(S)SMe	H	(94)

C_{32}		Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (83)	602

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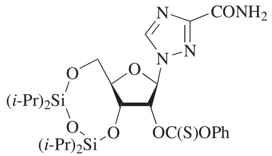
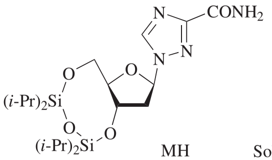
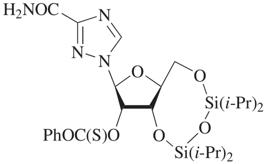
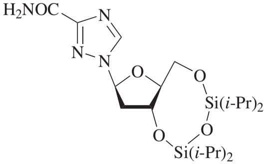
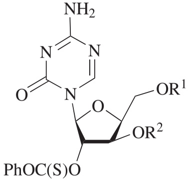
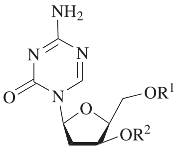
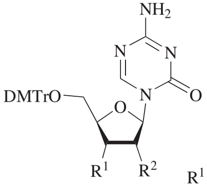
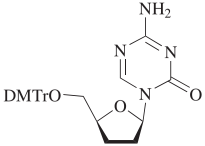
[a] This value gives the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value gives the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

[c] The yield was determined by NMR.

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	MH, AIBN, solvent	 MH — Solvent — Temp (°) Bu_3SnH — toluene — reflux — (79) $(TMS)_3SiH$ — dioxane — 80 — (68)[a]	 603 604
	Ph_3SiH, AIBN, dioxane, reflux, 12 h	 (50)	605
	$(TMS)_3SiH$, AIBN, dioxane, 100°, 2 h	 R^1 — R^2 Bz — Bz — (75)[a] —$Si(i\text{-}Pr)_2OSi(i\text{-}Pr)_2$— — (—)	606
 $R^1 = OC(S)Im; R^2 = H$ $R^1 = H; R^2 = OC(S)Im$	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (47)	607

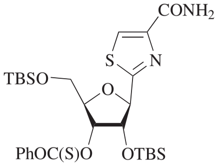
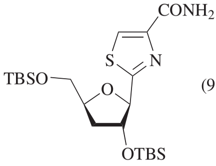
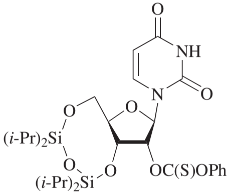
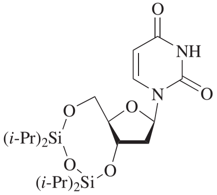
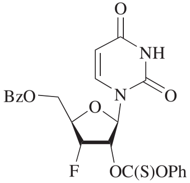
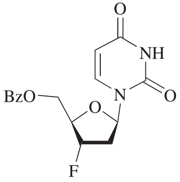
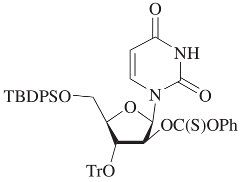
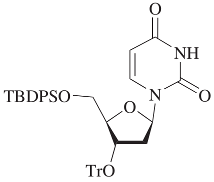
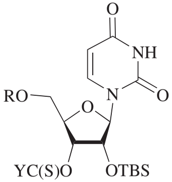
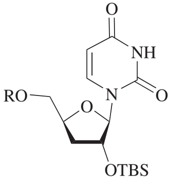
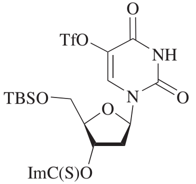
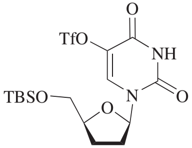
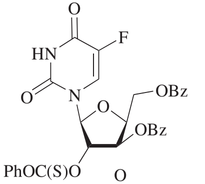
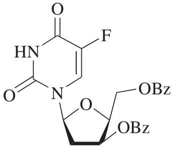
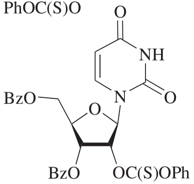
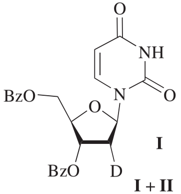
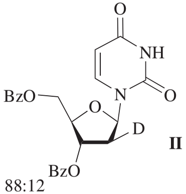
C_9			
	Bu_3SnH, AIBN, toluene, reflux, 1.25 h	 (92)	608
	Bu_3SnH, AIBN, toluene, 75°, 3 h	 (68)[b]	34
	Bu_3SnH, AIBN, toluene	 (54)	609
	Bu_3SnH, AIBN, toluene, 74–80°, 3h	 (27)	610

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	MH, AIBN, reflux, solvent		
		R · Y · MH · Solvent · Time (h)	
		DMTr · Im · Bu_3SnH · toluene · 3 · (55)	611
		Tr · PhO · Bu_3SnH · toluene-MeCN · 3 · (56)	612
		TBDMS · PhO · Ph_3SnH · toluene · 24 · (98)	613
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (79)	614
	$(TMS)_3SiH$, AIBN, dioxane, reflux, 2.5 h	 $(87)^a$	615
	Bu_3SnD, AIBN, diglyme, sonication, rt, 3 h	 **I** +  **II** **I + II** (55), **I**:**II** = 88:12	616, 617

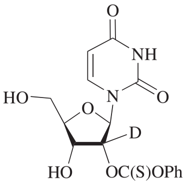
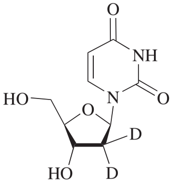
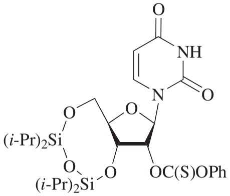
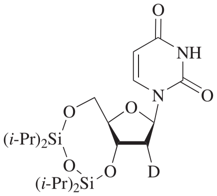
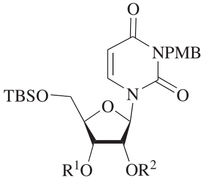
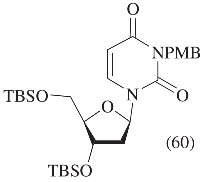
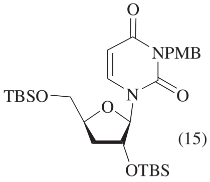
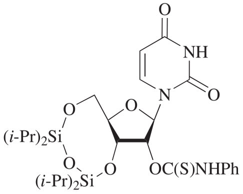
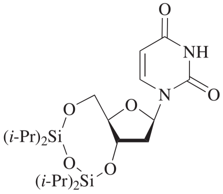
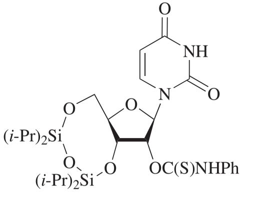
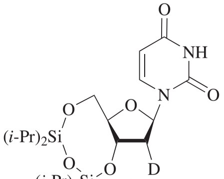
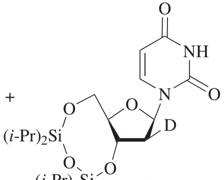
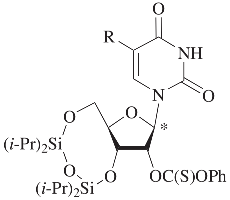
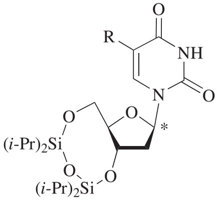
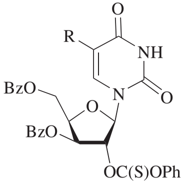
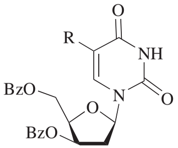
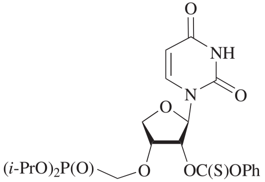
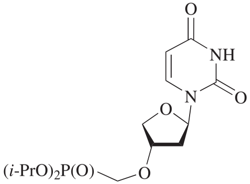
	Bu_3SnD, AIBN, diglyme, 80–100°, 0.5 h	**I + II** (80–90), **I**:**II** = 82:18–79:21	616
	Bu_3SnD, AIBN	 (—)	618
	$(TMS)_3SiD$, AIBN, benzene, reflux, 2 h	 (89), selectivity >99:1	45
 4:1 mixture R^1 = TBS; R^2 = C(S)SMe R^1 = C(S)SMe; R^2 = TBS	Bu_3SnH, AIBN, toluene, 90°, 1 h	 (60) +  (15)	619
	$(TMS)_3SiH$, AIBN, benzene, reflux, 2 h	 (93)	39

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	Bu_3SnD, AIBN, benzene, reflux, 4 h	 **I** +  **II** **I** + **II** (74), **I**:**II** = 86:14	39
C_{9-10}			
 * = ^{13}C R = H, Me	Bu_3SnH, AIBN, toluene, reflux	 (—)	620
	Bu_3SnH, AIBN, toluene, 80°, 24 h	 R H (71)^b Me (78)^b	621
C_9			
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (46)	622

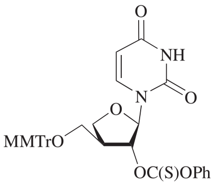
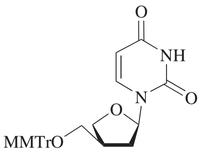
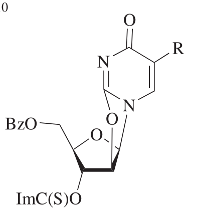
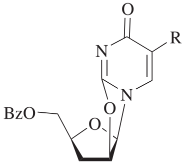
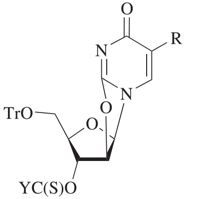
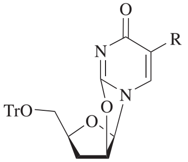
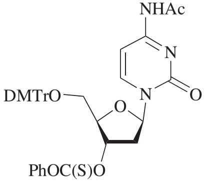
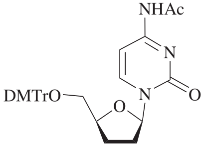
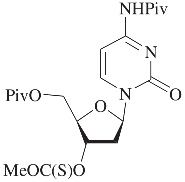
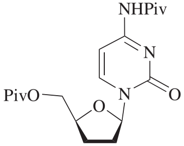
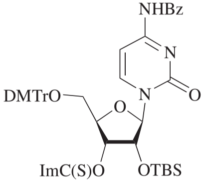
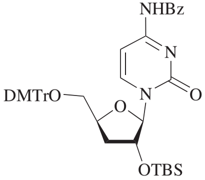
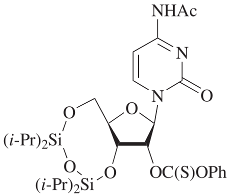
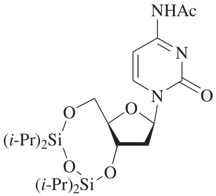
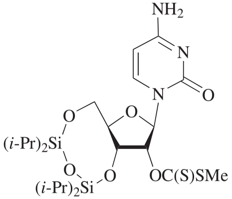
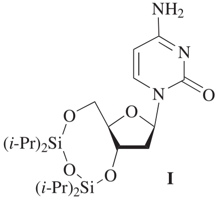
	Bu_3SnH, AIBN, benzene, reflux, 3 h		(80)	623
$C_{9–10}$				
	Bu_3SnH, AIBN, toluene–MeCN, reflux, 1 h		R H (73) Me (47)	624
	Bu_3SnH, AIBN, reflux		Y R Solvent Time (h) Im Me MeCN 1 (35)[a] PhO H toluene 6 (88)	625 612
C_9				
	Bu_3SnH, AIBN, toluene, reflux, 40 min		(78)	626

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	PMHS, $(Bu_3Sn)_2O$ (cat.), AIBN, toluene, reflux, 2 h	 (39)[b]	71
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (40)	611
	Bu_3SnH, AIBN, toluene, 75°, 14 h	 (74)[b]	34
	Diglyme (traces of peroxides), 100°, 4 h	 (trace)	212
	$(n\text{-}C_{11}H_{23}CO_2)_2$, *i*-PrOH, reflux	**I** (64)	212

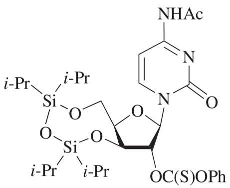
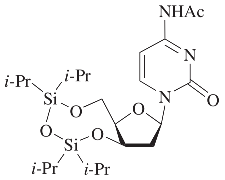
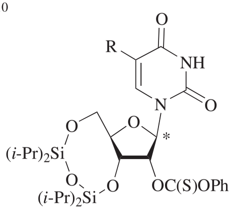
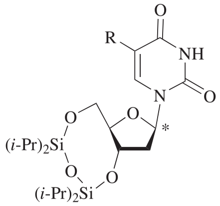
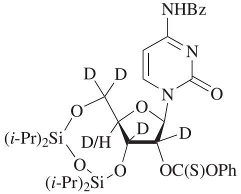
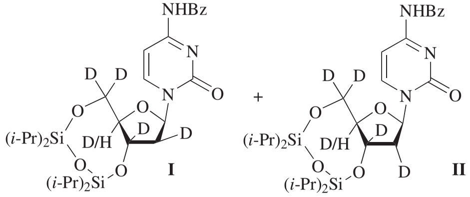
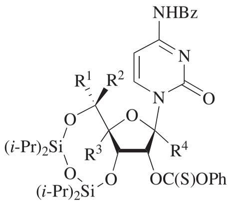
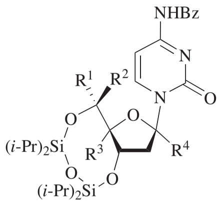
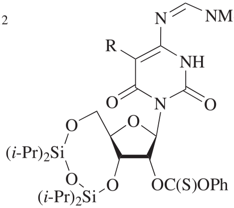
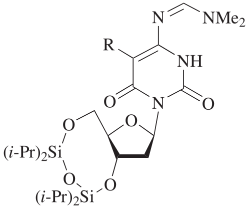
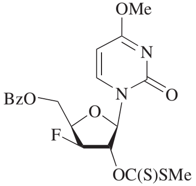
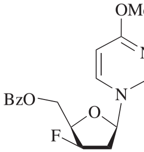
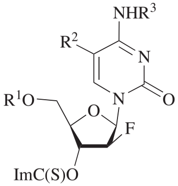
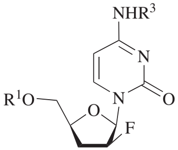
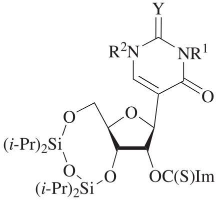
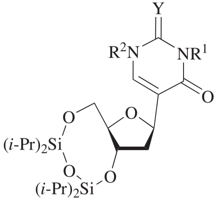
	Bu$_3$SnH, AIBN, toluene, 80°,		(50)^b	621
C_{9-10}				
 * = ^{13}C R = H, Me	Bu$_3$SnH, AIBN, toluene, reflux		(—)	620
C_9				
	Bu$_3$SnH, AIBN, toluene, 75°, 4 h	 **I** + **II** (70), **I**:**II** = 82:18		627
	Bu$_3$SnH, AIBN, toluene, 75°		R^1 R^2 R^3 R^4 H H H H (27)^b D D H H (26)^b H H D H (31)^b H H H D (31)^b D H H H (27)^b	628

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-12}		Bu_3SnH, AIBN, toluene, 75°, 1.5–2 h	 R: H (65) R: CH_2=$CHCH_2$ (58)	629
C_9		Diglyme (traces of peroxides), 100°, 4 h	 **I** (71)	212
		$(n\text{-}C_{11}H_{23}CO_2)_2$, *i*-PrOH, reflux	**I** (—)	212
	 R¹ R² R³: Tr I H Bz H Bz	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 R¹ R³: Tr H (74) Bz Bz (87)	114
		Bu_3SnH, AIBN, toluene, reflux, 1 h	 R¹ R² Y: H H NH (78) H H O (75) H Me O (74) Me Me O (65)	630

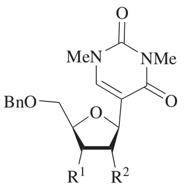
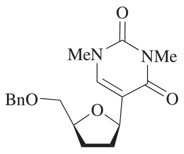
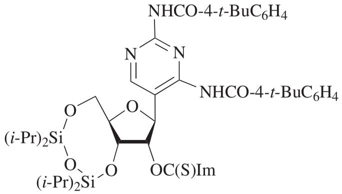
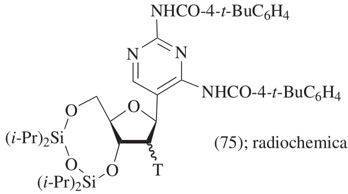
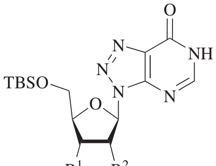
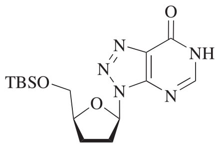
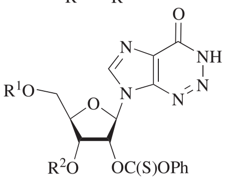
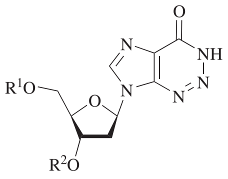
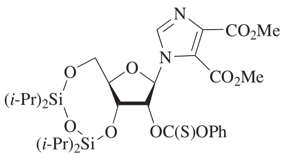
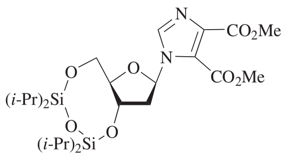
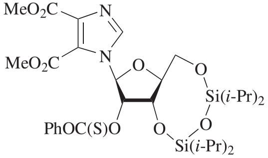
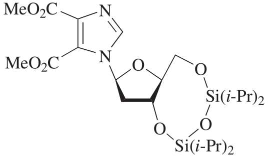
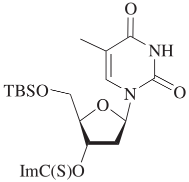
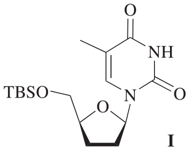
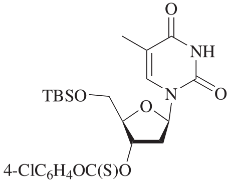
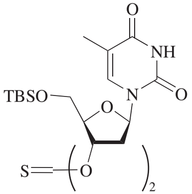
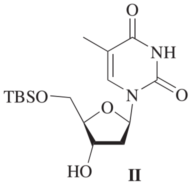
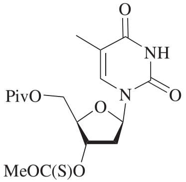
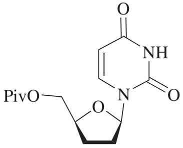
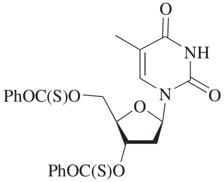
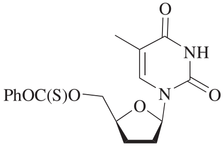
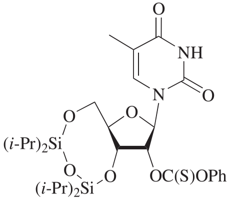
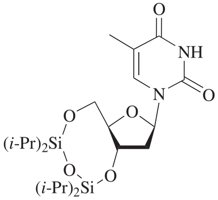
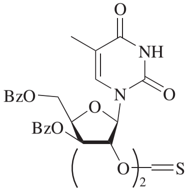
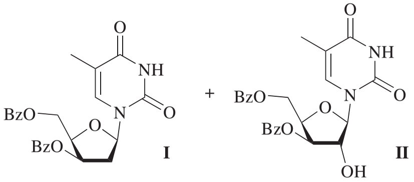
 $R^1 = H, R^2 = OC(S)OPh$ $R^1 = OC(S)OPh, R^2 = H$	Bu_3SnH, AIBN, toluene	 (92)	631
	Bu_3SnT, AIBN, toluene, reflux, 1 h	 (75); radiochemical (50)	632
 $R^1 = H, R^2 = OC(S)Im$ $R^1 = OC(S)Im, R^2 = H$	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (54)[a]	234
	Bu_3SnH, AIBN, toluene, 75°, 3 h	 R^1 — R^2 DMTr — TBS (55) —$(i\text{-}Pr)_2SiOSi(i\text{-}Pr)_2$— (60)	633
C_{10}			
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (>95)	634

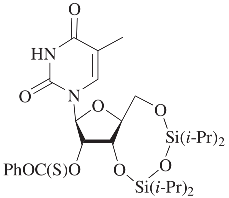
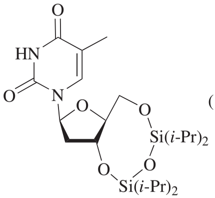
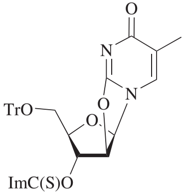
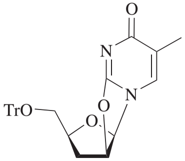
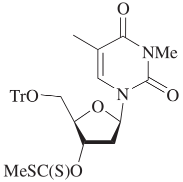
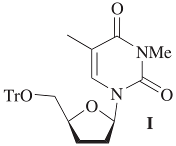
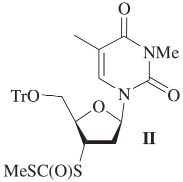
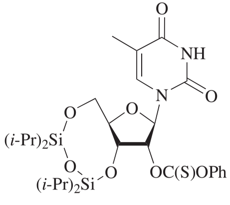
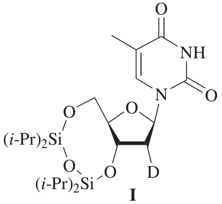
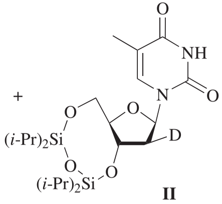
TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (>95)	635
	Bu_3SnH, AIBN, dioxane, reflux, 6 h	 **I** (75)^b	636
	Ph_3SiH, Bz_2O_2, toluene, reflux, 6 h	**I** (80)	37
	Ph_3SiH, Bz_2O_2, solvent, reflux	**I** +  **II** Solvent / Time (h) / **I** / **II** toluene / 20 / (85) / (10) dioxane / 3 / (75) / (22)	37

	PMHS, $(Bu_3Sn)_2O$ (cat.), AIBN, toluene, reflux, 2 h		$(90)^b$	71
	Bu_3SnH (1.2 eq), AIBN, benzene, reflux, 1.5 h		(63)	26
	Bu_3SnH, AIBN, toluene, reflux, 3 h		(67)	637
	Ph_3SiH, Bz_2O_2, solvent, reflux			37

Solvent	Time (h)	**I**	**II**
toluene	25	(70)	(25)
dioxane	3	(45)	(39)

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, 80–90°	 (82)	638
	Bu_3SnH, AIBN, toluene–MeCN, reflux, 5 h	 (35)[a]	625
	Solvent, $(n\text{-}C_{11}H_{23}CO_2)_2$, collidine, solvent, reflux Solvent / I / II *i*-PrOH / (45) / (11) benzene / (31) / (60)	 **I** +  **II**	32
	Bu_3SnD, AIBN, toluene, 85°	 **I** +  **II** **I** + **II** (66), **I**:**II** = 85:15	639

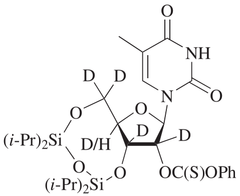
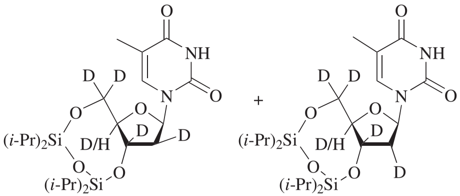
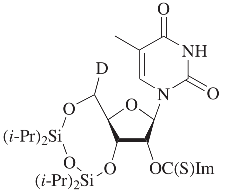
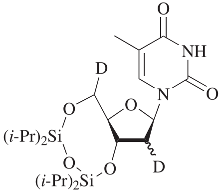
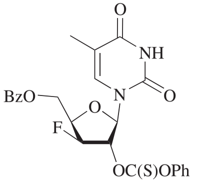
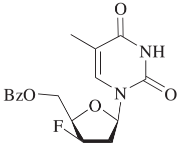
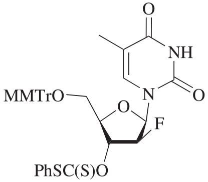
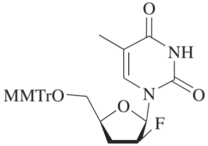
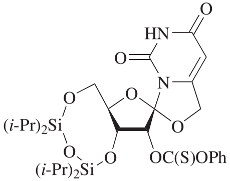
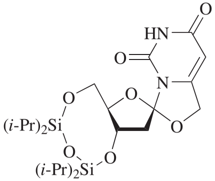
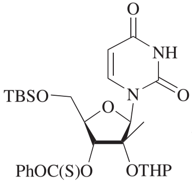
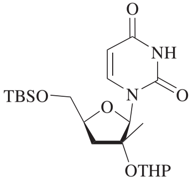
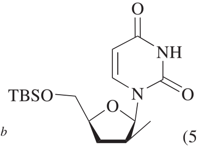
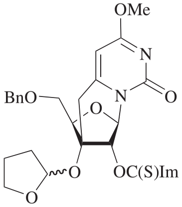
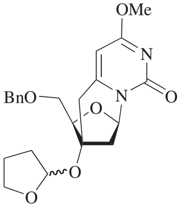
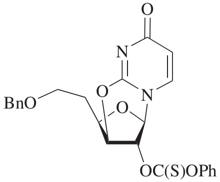
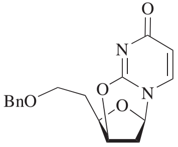
	(TMS)$_3$SiD, Et$_3$B, O$_2$, TMTHF, 0°	**I** + **II** (81), **I**:**II** > 99:1	45
	Bu$_3$SnD, AIBN, toluene, 75°, 3.5 h	 **I** **II** **I** + **II** (86), **I**:**II** = 89:11	627
	Bu$_3$SnD, AIBN, toluene, 85°	 (—)	639
	Bu$_3$SnH, AIBN, toluene, 80°, 2 h	 (25)^a	640
	Bu$_3$SnH, AIBN, toluene, 75°, 2 h	 (57)^a	641

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	$(TMS)_3SiH$, AIBN, toluene, 80°, 6 h	 (94)	179
 crude mixture	$(TMS)_3SiH$, toluene, reflux	 (22)[b] +  (56)[b]	642
	Bu_3SnH, AIBN, toluene, 100°, 1.5 h	 (43)	643
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 (89)	644

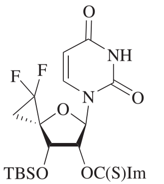
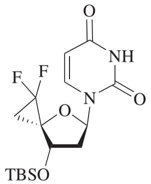
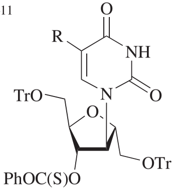
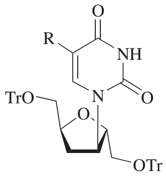
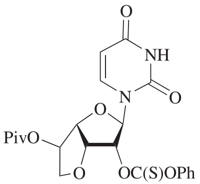
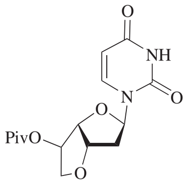
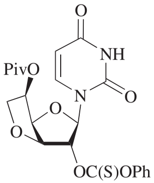
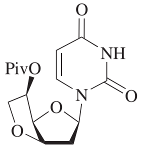
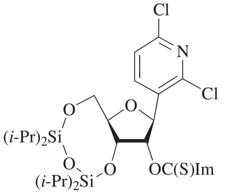
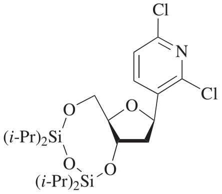
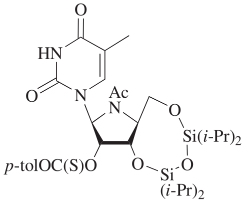
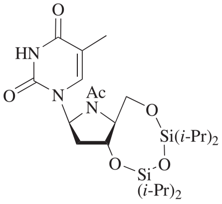
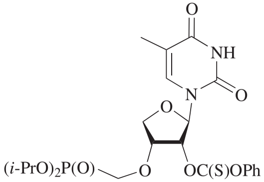
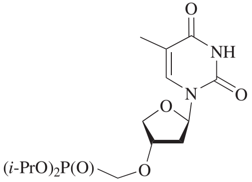
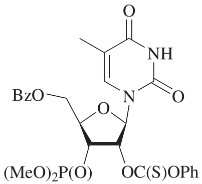
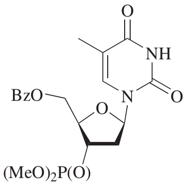
	Bu$_3$SnH, AIBN, toluene, 90°, 1 h	 (64)	619
C_{10-11}			
	Bu$_3$SnH, AIBN, benzene, reflux, 1.5 h	 R H (40)[a] Me (51)[a]	645
C_{10}			
	Bu$_3$SnH, AIBN, toluene, reflux	 (80)	646
	Bu$_3$SnH, AIBN, toluene, reflux, 1 h	 (63)[a]	646

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, 80°	 (85)	647
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (80)	386
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (64)	622
	Bu_3SnH, AIBN, toluene, 80°, 1 h	 (83)	648

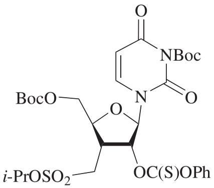
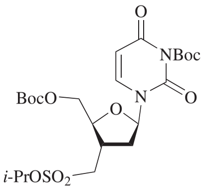
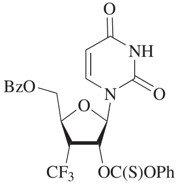
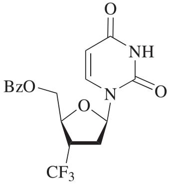
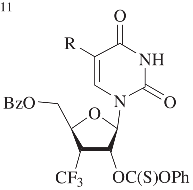
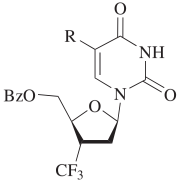
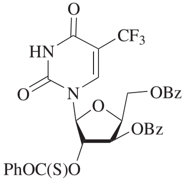
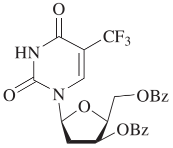
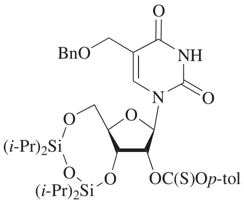
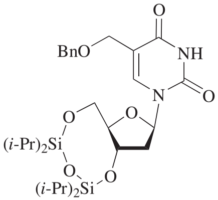
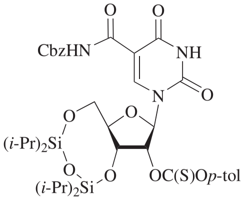
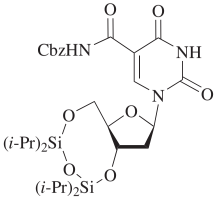
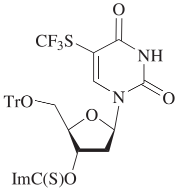
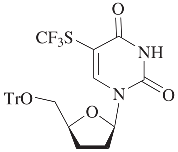
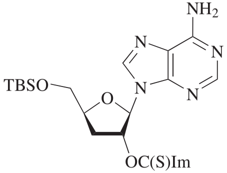
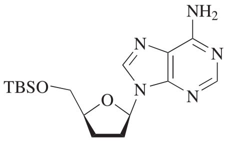
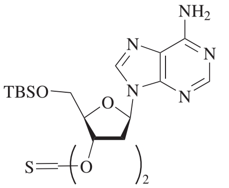
		Bu_3SnH, AIBN, toluene, 100°, 3 h		(48)^a	649
		$(TMS)_3SiH$, AIBN, toluene, reflux, 17 h		(80)^a	650
$C_{10–11}$		Bu_3SnH, AIBN, toluene, reflux, 2 h		R H (76) Me (80)	651
C_{10}		$(TMS)_3SiH$, AIBN, dioxane, reflux, 0.5 h		(92)^a	652

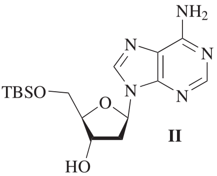
TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, 80°, 2.5 h	 (91)[a]	653
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (71)[a]	654
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (43)[b]	95
	Bu_3SnH, AIBN, toluene, reflux	 (63) **I**	655



Ph$_3$SiH, Bz$_2$O$_2$, solvent, reflux

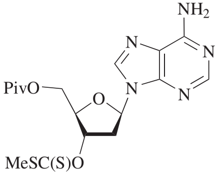
I +



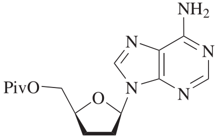
II

Solvent	Time (h)	**I**	**II**
toluene	25	(75)	(8)
dioxane	4	(54)	(36)

37

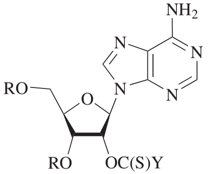


PMHS, (Bu$_3$Sn)$_2$O (cat.), AIBN, toluene, reflux, 2 h

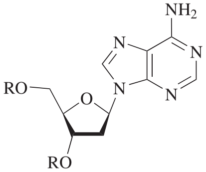


(88)^b

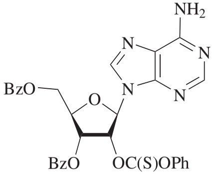
71



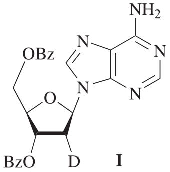
Bu$_3$SnH, AIBN, toluene



R	Y	Temp (°)	Time (h)		
TBS	OPh	100	12	(75)	656
Bz	Ph	reflux	2	(89)	657

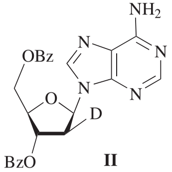


Bu$_3$SnD, AIBN, toluene, 100°



I

+

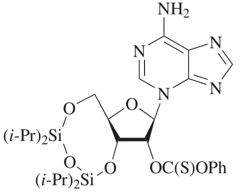
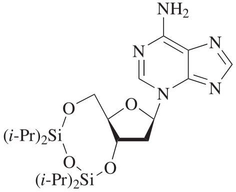
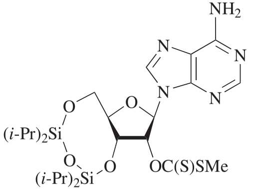
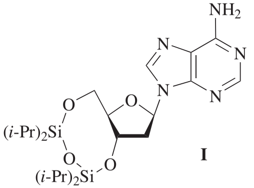
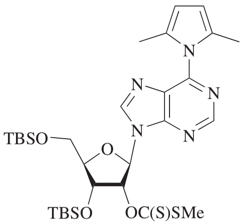
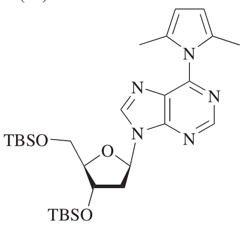
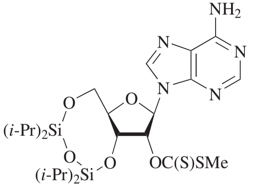
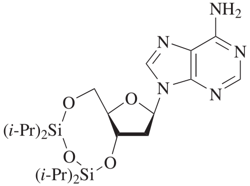


II

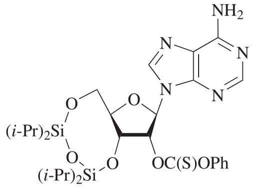
I + **II** (93), **I**:**II** = 74:26

617

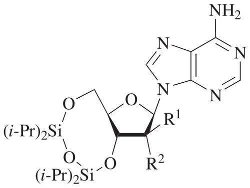
TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, 75°, 6 h	 (76)	658
	Diglyme (traces of peroxides), 100°, 4 h	 **I** (23)	212
C_{16}	$(n\text{-}C_{11}H_{23}CO_2)_2$, *i*-PrOH, reflux	**I** (75)	212
	Bu_3SnH, AIBN, toluene, 100°, 1 h	 (93)	619
C_{10} 	MH, AIBN, solvent		

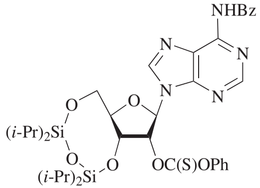
MH	Solvent	Temp (°)	Time (h)		
Bu_3SnH	toluene	75	3	(75)[b]	66, 34
$(TMS)_3SiH$	benzene	reflux	2	(80)	659
$(TMS)_3SiH$	benzene	reflux	2	(97)	39



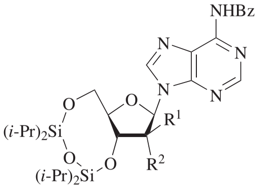
Bu_3SnD, AIBN,
toluene, 75°, 3 h



	R^1	R^2	I + II	I:II	
I	H	D	(89)[b]	88:12	34
II	D	H	(87)	88:12	617



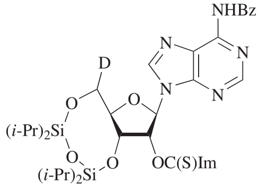
Bu_3SnD, AIBN, toluene, 85°



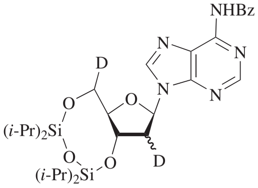
	R^1	R^2
I	H	D
II	D	H

I + II (45), **I**:**II** = 85:15

639



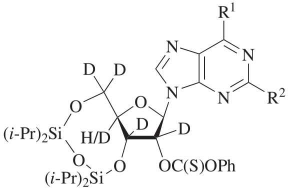
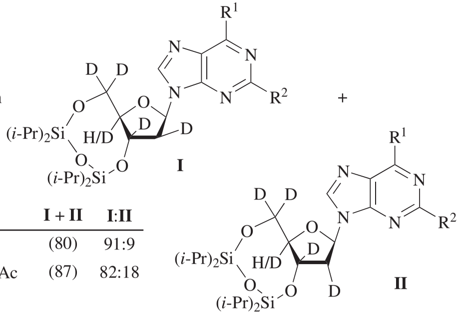
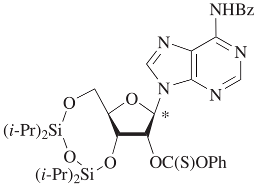
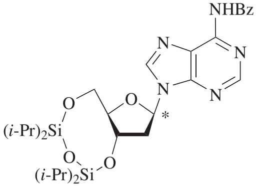
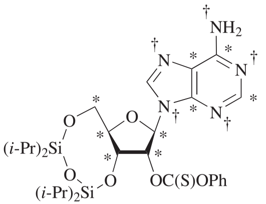
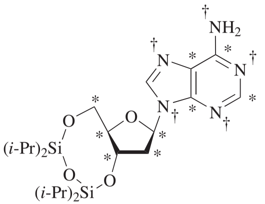
Bu_3SnD, AIBN, toluene, 85°



(—)

639

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		Bu_3SnH, AIBN, toluene, 75°, 3.5 h	 I + II	627
	 * = ^{13}C	Bu_3SnH, AIBN, toluene, reflux	 (—)	620
	 * = ^{13}C † = ^{15}N	Bu_3SnH, AIBN	 (—)	660

R^1	R^2	**I + II**	**I:II**
NHBz	H	(80)	91:9
ODPC	NHAc	(87)	82:18

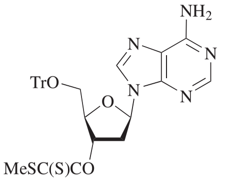
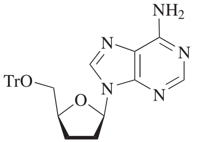
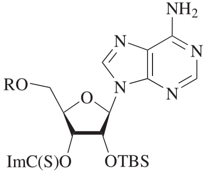
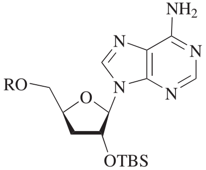
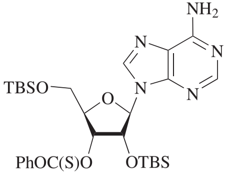
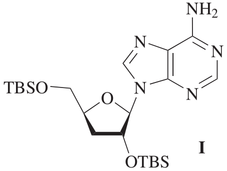
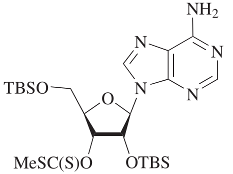
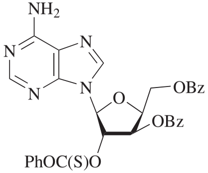
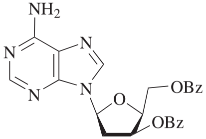
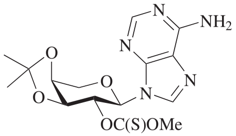
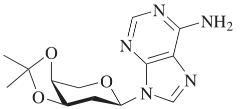
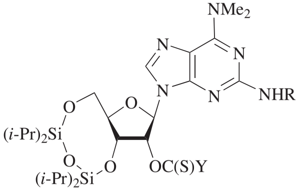
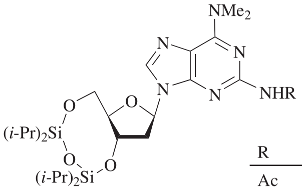
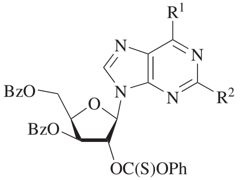
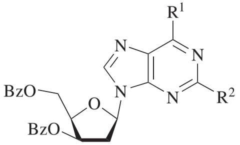
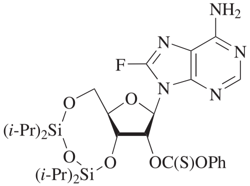
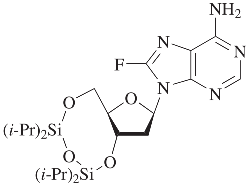
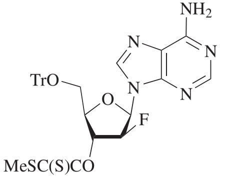
	H_3PO_2 (5 eq), Et_3N (10 eq), AIBN (0.3 eq), DME, reflux, 1 h	 (79)	195
	Bu_3SnH, AIBN, toluene, reflux	 R TBS (87) DMTr (42)	655 611
	Bu_3SnH, AIBN, toluene, 100°, 12 h	 **I** (80)	656
	Polystyrene-linked Bu_2SnH, AIBN, toluene, 80°	**I** (81)^b	104
	$(TMS)_3SiH$, AIBN, dioxane	 (96)	661

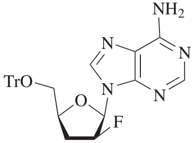
TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, 80°, 2 h	 (92)	662
	Bu_3SnH, AIBN	 R — Y Ac — OPh — $(81)^b$ Bz — OPh — $(65)^b$ $COCH_2OPh$ — Im — (98)	 663 663 664
	Bu_3SnH, AIBN, toluene, 80°	 R^1 — R^2 — Time (h) NH_2 — H — 8 — $(77)^b$ OTMS — NHAc — 36 — $(31)^b$	621
	MH, initiator, solvent		665

Y	MH	Initiator	Solvent	Temp (°)	Time (h)	
Im	$(TMS)_3SiH$	$(t\text{-}Bu)_2O_2$	toluene	80	0.25	(84)
Im	Et_3SiH	Bz_2O_2	toluene	110	1.75	(60)
Im	$(TMS)_3SiH$	Et_3B	benzene	rt	48	(60)
SCH_2CH_2CN	$(TMS)_3SiH$	Et_3B	benzene	rt	48	(72)

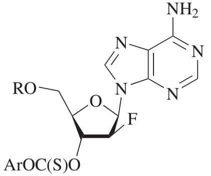


MH, AIBN, amine,
DME, reflux, 2 h

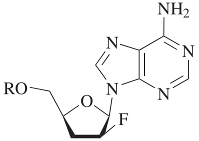


MH	Amine	
$(MeO)_2P(O)H$	—	(84)
$(EtO)_2P(O)H$	—	(82)
H_3PO_2	Et_3N	(93)

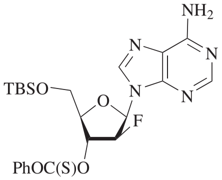
195



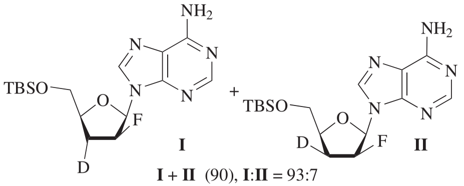
MH, AIBN, solvent



R	Ar	MH	Solvent	Temp (°)	Time (h)		
Tr	Ph	$(TMS)_3SiH$	toluene	100	—	(73)	666
Tr	Ph	$(TMS)_3SiH$	toluene	reflux	—	(78)	667, 668
Tr	Ph	Ph_2SiH_2	dioxane	reflux	—	(81)	667, 668
Tr	Ph	Ph_2MeSiH	dioxane	reflux	—	(69)	667, 668
Tr	$4\text{-}FC_6H_4$	Et_3SiH	dioxane	reflux	1	(55)	667
TBS	Ph	Bu_3SnH	toluene	90	1	(71)	669



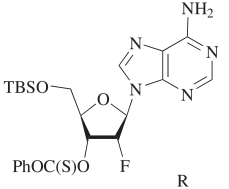
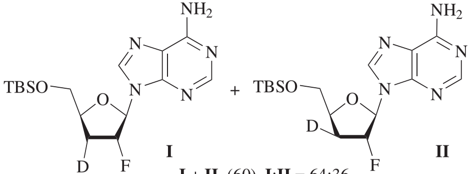
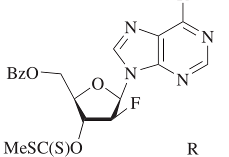
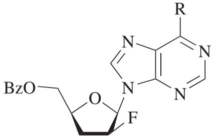
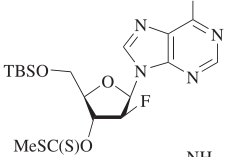
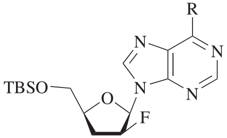
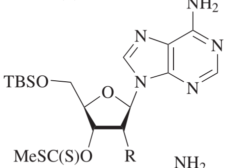
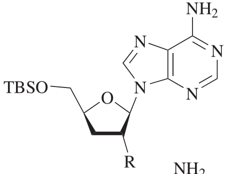
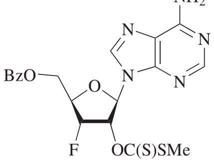
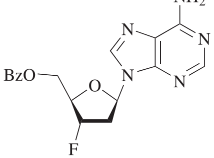
Bu_3SnD, AIBN,
toluene, 85°, 3 h



I + **II** (90), **I**:**II** = 93:7

48

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		Bu_3SnD, AIBN, toluene, 85°, 3 h	 **I** + **II** (60), **I**:**II** = 64:36	99
		**A**: Diglyme (traces of peroxides), 100°, 4 h **B**: (n-$C_{11}H_{23}CO_2)_2$, collidine, *i*-PrOH, reflux	 R **A** **B** OMe (74) (81) Cl (76) (—)	212
		**A**: Diglyme (traces of peroxides), 100°, 4 h **B**: (n-$C_{11}H_{23}CO_2)_2$, collidine, *i*-PrOH, reflux	 R **A** **B** OMe (91) (94) NH_2 (31) (86)	212
		**A**: Diglyme (traces of peroxides), 100°, 4 h **B**: (n-$C_{11}H_{23}CO_2)_2$, collidine, *i*-PrOH, reflux	 R **A** **B** H (6) (63) F (7) (84)	212
		**A**: Diglyme (traces of peroxides), 100°, 4 h **B**: (n-$C_{11}H_{23}CO_2)_2$, collidine, *i*-PrOH, reflux	 **A** **B** (64) (82)	212

C_{10}

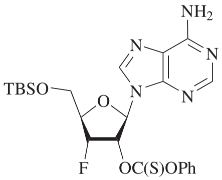
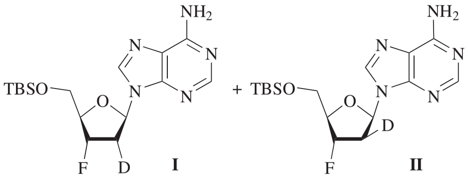
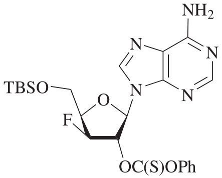
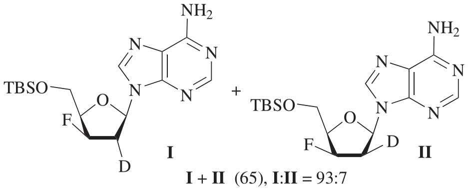
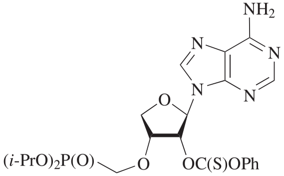
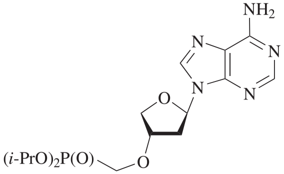
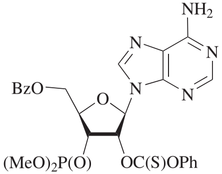
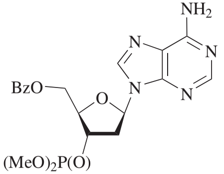
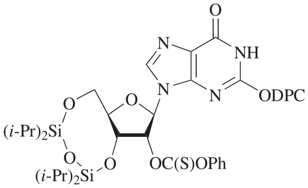
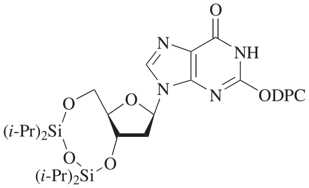
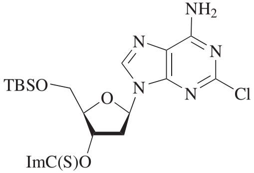
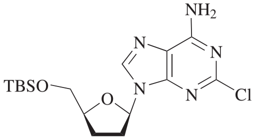
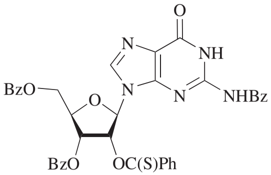
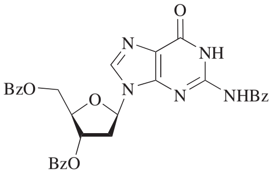
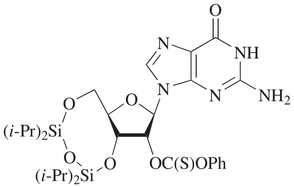
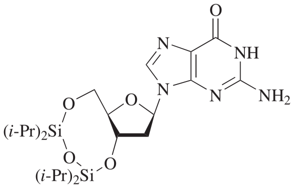
	Bu_3SnD, AIBN, toluene, 85°, 3 h	 **I** + **II** (54), **I**:**II** = 85:15	48
	Bu_3SnD, AIBN, toluene, 85°, 3 h	 **I** + **II** (65), **I**:**II** = 93:7	48
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (23)	622
	Bu_3SnH, AIBN, toluene, 80°, 1 h	 (52)	648

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Bu_3SnH, AIBN, toluene	 (82)	670
	$(TMS)_3SiH$, AIBN, dioxane, reflux	 (—)	671
	Bu_3SnH, toluene, reflux, 2 h	 (85)	657
	Bu_3SnH, AIBN, toluene, 75°, 3 h	 (86)^b	34

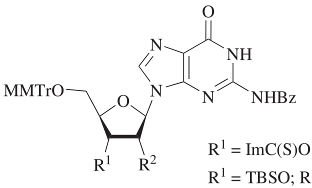
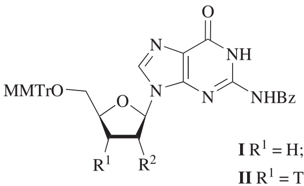
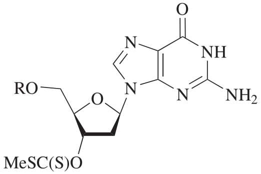
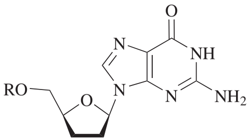
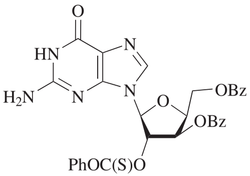
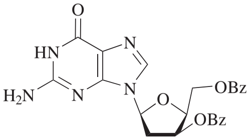
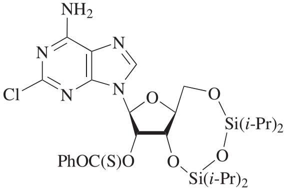
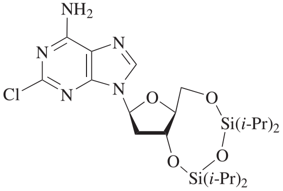
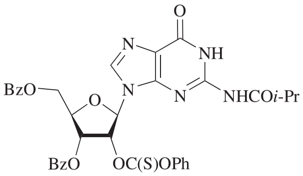
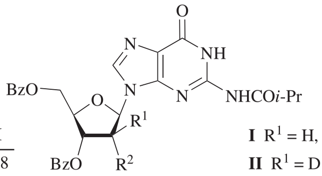
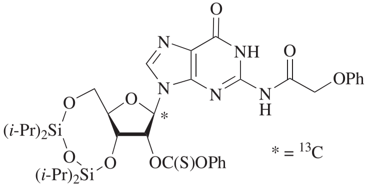
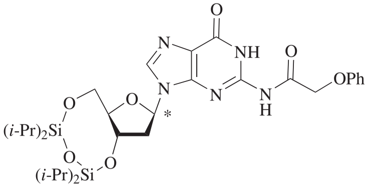
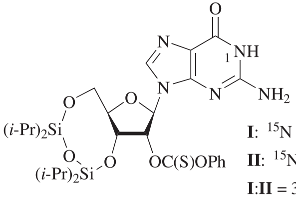
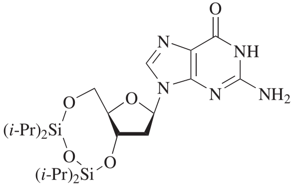
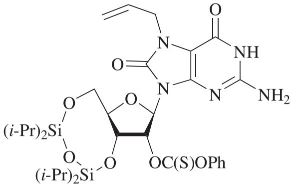
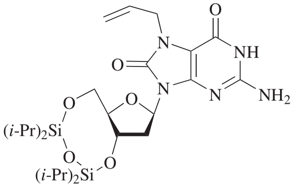
 R^1 = ImC(S)O; R^2 = TBSO R^1 = TBSO; R^2 = ImC(S)O	Bu_3SnH, AIBN, toluene, reflux, 4 h	 **I** + **II** (41) **I** R^1 = H; R^2 = TBSO **II** R^1 = TBSO, R^2 = H	661
	PMHS, $(Bu_3Sn)_2O$ (cat.), AIBN, reflux, 2 h	 R Solvent Ac dioxane (85)[b] Piv toluene (65)[b]	71
	$(TMS)_3SiH$, AIBN, dioxane, reflux, 1 h	 (65)	672
	$(TMS)_3SiH$, AIBN, toluene, reflux, 3 h	 (93)[a]	673

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Bu_3SnD, AIBN Temp (°) — I:II 65 — 52:48 12 sonication 64:36	 (—) **I** $R^1 = H, R^2 = D$ **II** $R^1 = D, R^2 = H$	674
 * = ^{13}C	Bu_3SnH, AIBN, toluene, reflux	 (—)	620
 **I**: ^{15}N at N-1 **II**: ^{15}N at NH_2 **I**:**II** = 3:1	Bu_3SnH, AIBN, toluene, 75°, 3 h	 (84)	675
	Bu_3SnH, AIBN, toluene, reflux, 20 h	 (60)	676

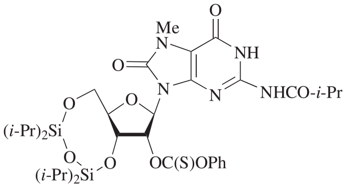
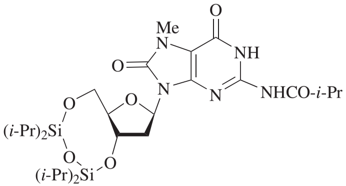
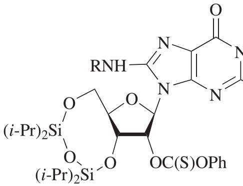
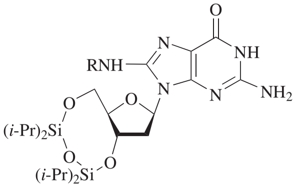
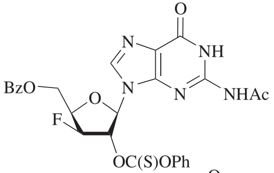
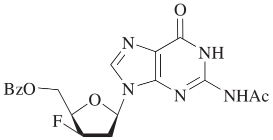
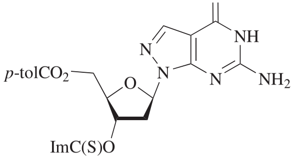
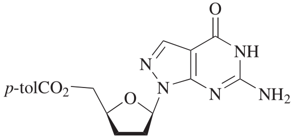
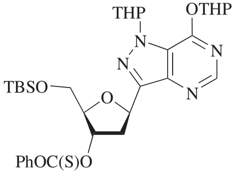
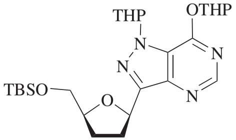
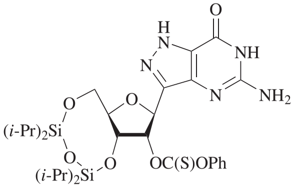
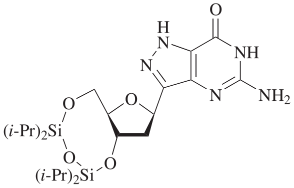
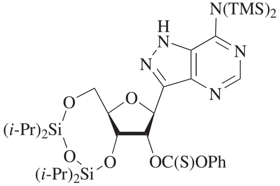
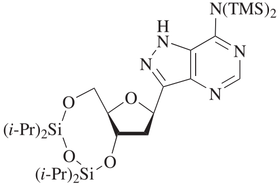
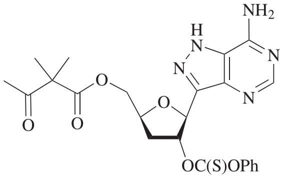
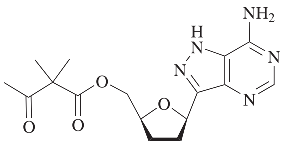
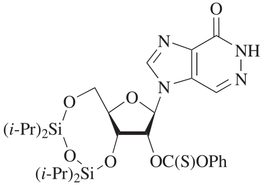
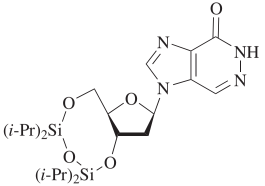
	Bu$_3$SnH, AIBN, toluene, 70°, 1.5 h		(50)^a	677
 R = Ph, 2-fluorenyl	Bu$_3$SnH, AIBN, toluene		(—)	678
	Bu$_3$SnH, AIBN, toluene, 80°, 2 h		(79)^a	640
	Bu$_3$SnH, AIBN, toluene, 100°, 2 h		(93)	679
	Bu$_3$SnH, AIBN, toluene, 80°, 15 h		(80)	680

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Polystyrene-linked Bu_2SnH, AIBN, toluene, 80°, 1.5 h	 (92)	681
	Bu_3SnH, AIBN, toluene, 75°, 24 h	 (53)	682
	Bu_3SnH, AIBN, benzene, reflux, 70 min	 (93)	683
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (98)	684

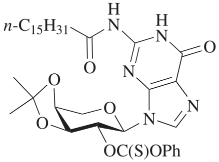
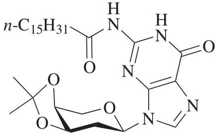
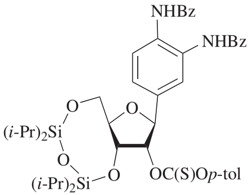
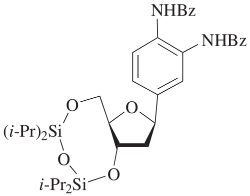
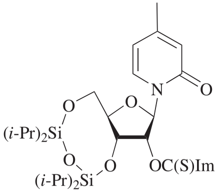
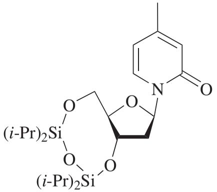
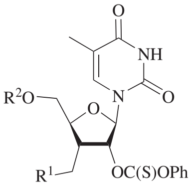
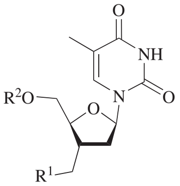
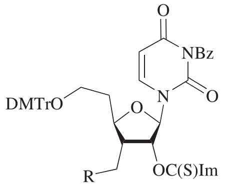
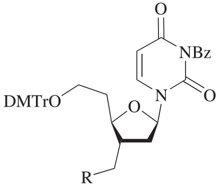
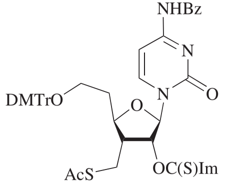
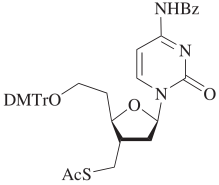
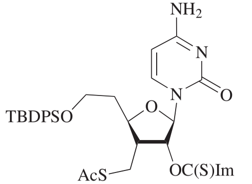
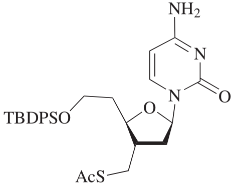
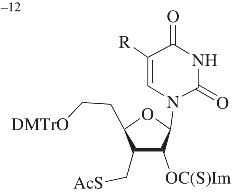
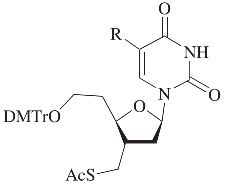
	Bu$_3$SnH, AIBN, toluene, reflux		(61)	662
C$_{11}$				
	Bu$_3$SnH, AIBN, toluene, 80°		(99)	685
	Bu$_3$SnH, AIBN, toluene, reflux, 1.5 h		(—)	686
	Bu$_3$SnH, AIBN, toluene, 100°, 5 h		R^1 R^2 F Bn (85) BnO Bn (47) N$_3$ TMS (43)	122

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	Bu_3SnH, AIBN, toluene, reflux, 8 min	 R: BzO (—) AcS (86)	687
	Bu_3SnH, AIBN, toluene, reflux, 8 min	 (86)	687
	Bu_3SnH, AIBN, toluene, reflux	 (86)	94
C_{11-12}			
 R = H, Me	Bu_3SnH, AIBN, toluene, reflux	 (85–90)	94

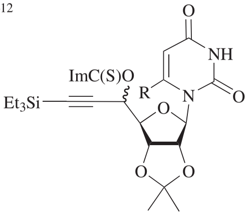
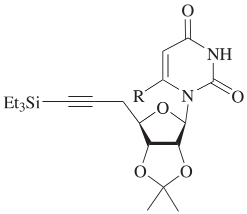
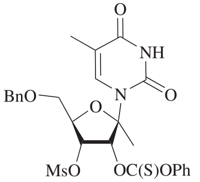
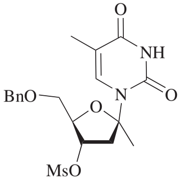
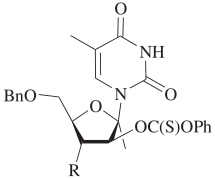
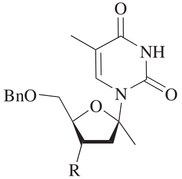
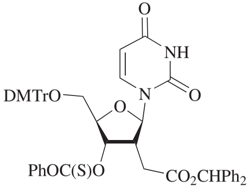
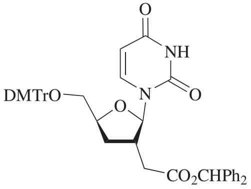
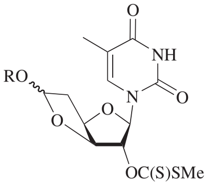
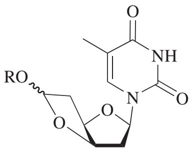
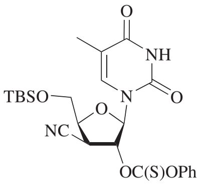
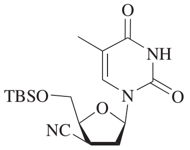
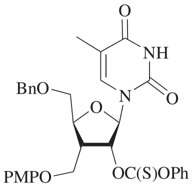
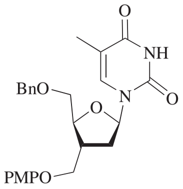
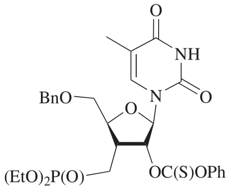
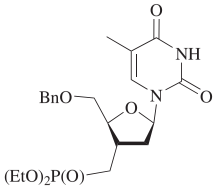
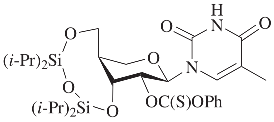
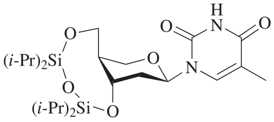
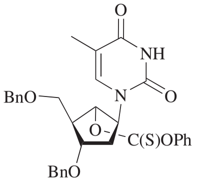
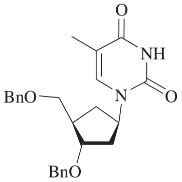
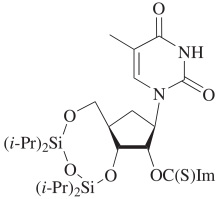
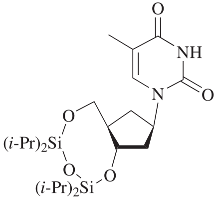
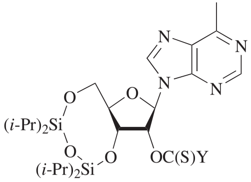
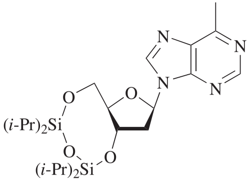
C_{11-12}			
	Bu_3SnH, AIBN, toluene, 80°, 1.5 h	 R H (81)[a] $TBSOCH_2$ (59)[a]	688
C_{11}			
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (74)	123
 R N_3 H	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 R NH_2 (43) H (76)	123
	Bu_3SnH, AIBN, toluene, 56°, 8 h	 (88)	689

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

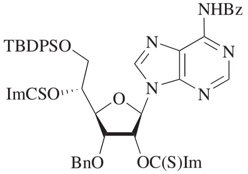
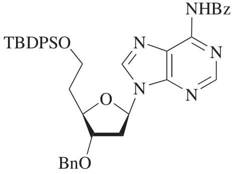
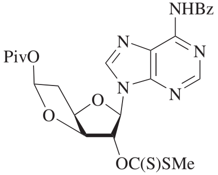
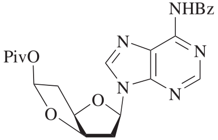
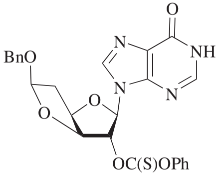
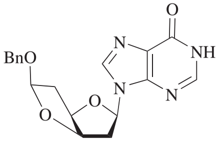
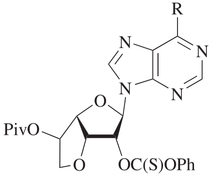
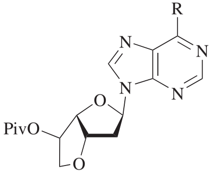
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	Bu_3SnH, AIBN, toluene, reflux, 4–5 h	 R Me (65) Bn (72)	 690 691
	Bu_3SnH, AIBN, toluene	 (55)	692, 693
	Bu_3SnH, AIBN, toluene, 100°, 1 h	 (63)[a]	694
	Bu_3SnH, AIBN, toluene, 70°, 1 h	 (82)	695

C_{11}

	Bu_3SnH, AIBN, toluene, 90°, 2 h		(79)	696
	Bu_3SnH, AIBN, toluene, 3.5 h		(55)[a]	260
	Bu_3SnH, AIBN, toluene, 70°		(67)	259
	MH, initiator, toluene			

Y	MH	Initiator	Temp (°)	Time (h)		
OPh	Bu_3SnH	AIBN	75	2	(98)	697
Im	Et_3SiH	Bz_2O_2	reflux	1.5	(55)[a]	698

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	Bu_3SnH, AIBN, toluene, 75°, 2 h	 (80)	699
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 $(80)^a$	646
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 $(42)^a$	646
 R = Cl, NHBz	Bu_3SnH, AIBN, toluene, reflux	 $(42)^a$	646

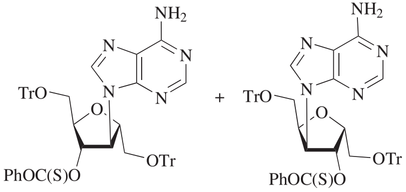
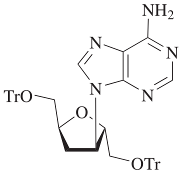
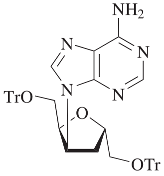
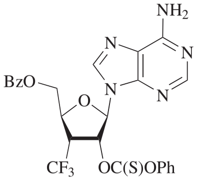
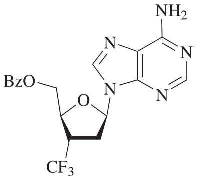
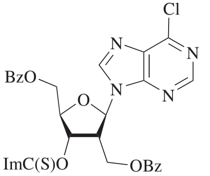
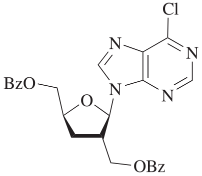
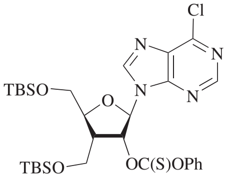
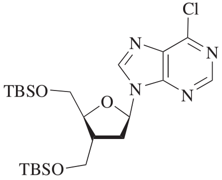
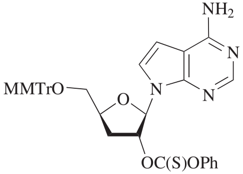
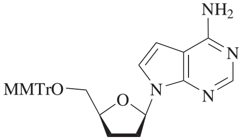
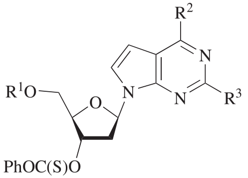
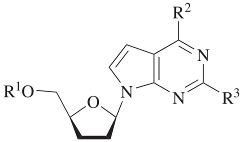
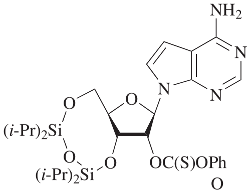
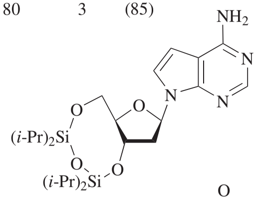
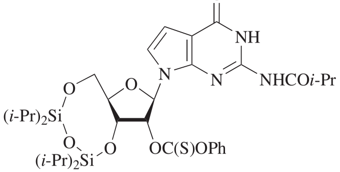
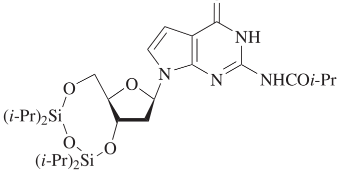
	Bu$_3$SnH, AIBN, benzene, reflux, 4 h	 (52)^a +  (17)^a	645
	(TMS)$_3$SiH, AIBN, toluene, reflux, 4 h	 (70)^a	650
	Bu$_3$SnH, AIBN, toluene, 85°, 5 min	 (72)	700
	Bu$_3$SnH, AIBN, toluene, reflux, 3 h	 (75)	700

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		Bu_3SnH, AIBN, benzene, reflux, 1.5 h	 (90)	683
		Bu_3SnH, AIBN, toluene		

R^1	R^2	R^3	Temp (°)	Time (h)		Refs.
Tr	OMe	SMe	105	0.2	(85)	701
Piv	Cl	H	reflux	0.2	(81)	701
DMTr	Cl	H	75	2	(75)	702
DMTr	Cl	Cl	80	3	(85)	702

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bu_3SnH, AIBN, toluene, 75°, 3 h	 $(68)^b$	34
		Bu_3SnH, AIBN, toluene, 60°, 4 h	 (90)	703

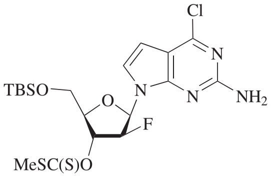
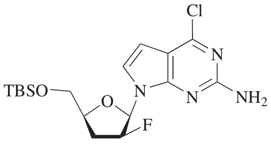
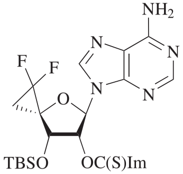
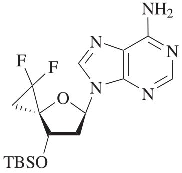
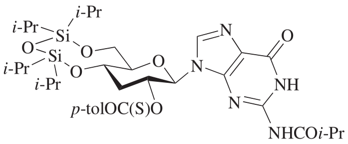
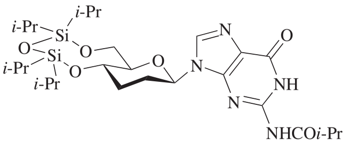
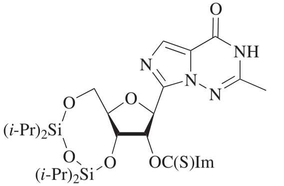
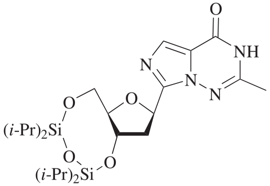
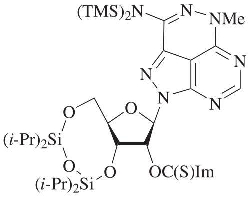
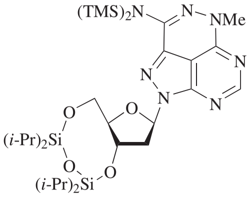
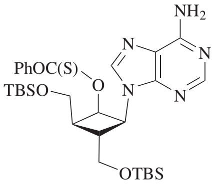
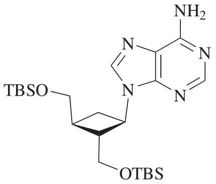
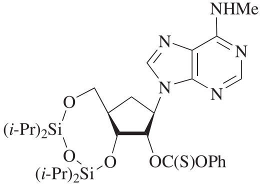
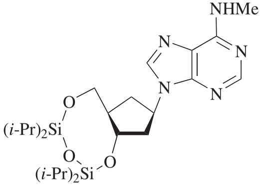
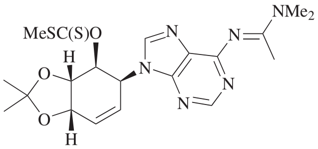
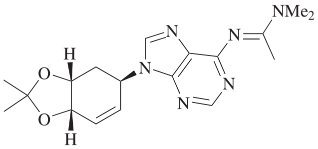
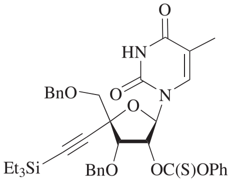
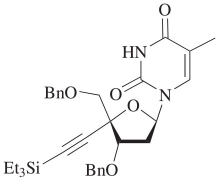
	Bu$_3$SnH, AIBN, toluene, 80°, 3 h		(90)	704
	Bu$_3$SnH, AIBN, toluene, 90°, 1 h		(31)	619
	Bu$_3$SnH, AIBN, toluene, 75°, 3 h		(36)^b	705
	Bu$_3$SnH, AIBN, toluene, reflux, 1 h		(91)	706
	Bu$_3$SnH, AIBN, toluene, reflux, 2.5 h		(61)^b	707

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	Bu_3SnH, AIBN, dioxane, reflux, 0.5 h	 (73)	262
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (82)	261
	Bu_3SnH, AIBN, dioxane, reflux, 4 h	 (80)	708
C_{12}			
	Bu_3SnH, AIBN, toluene, 85°, 1 h	 (95)[a]	709

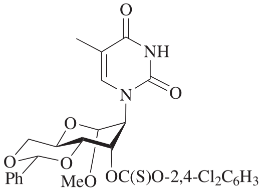
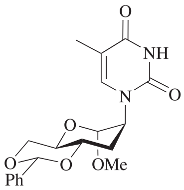
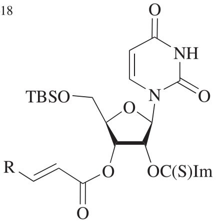
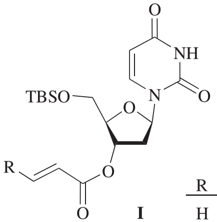
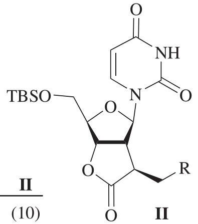
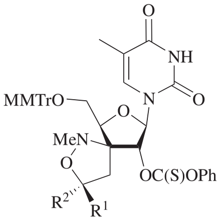
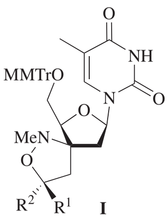
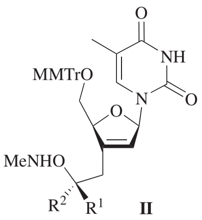
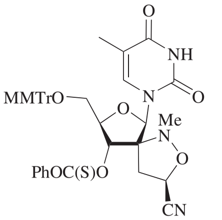
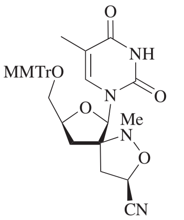
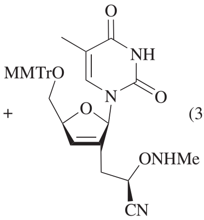
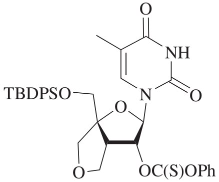
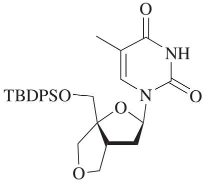
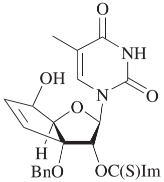
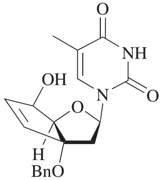
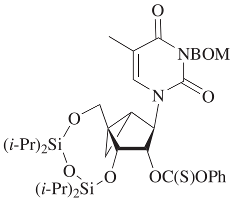
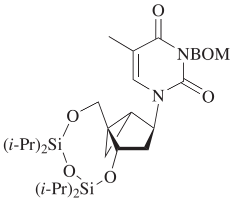
C_{11}		Bu_3SnH, AIBN, toluene, 80°	 (85)	710
C_{12-18}		Bu_3SnH (added over 24 h), benzene, reflux	 **I** +  **II** R | **I** | **II** H | (13) | (10) Me | (50) | (20) Ph | (35) | (35)	711
C_{12-13}		Bu_3SnH, AIBN, toluene, 100°, 1 h	 **I** +  **II** R^1 | R^2 | **I** | **II** H | EtO | (22) | (30) CN | H | (30) | (45)	137

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		Bu_3SnH, AIBN, toluene, 100°, 30 min	 (20) +  (30)	137
		Bu_3SnH, AIBN	 (48)[a]	712
		Bu_3SnH, AIBN, MeCN	 (61)[a]	713, 714
		Bu_3SnH, AIBN, DME, 80°, 3 h	 (65)	715

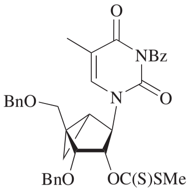
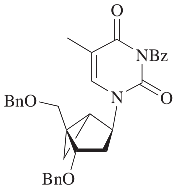
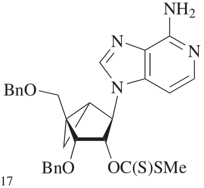
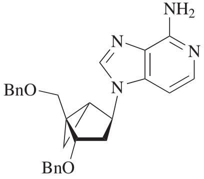
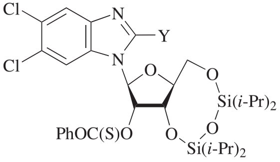
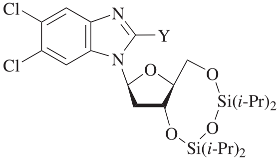
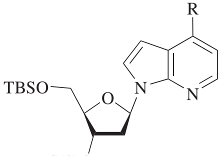
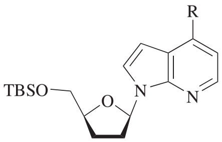
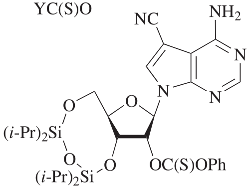
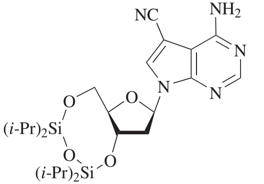
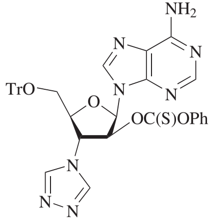
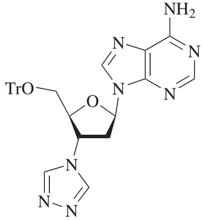
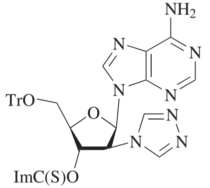
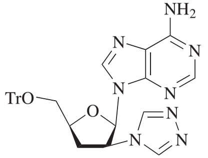
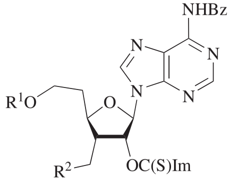
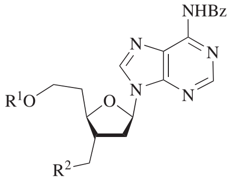
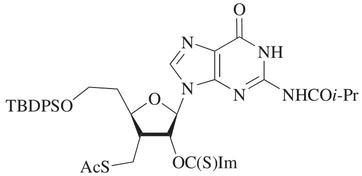
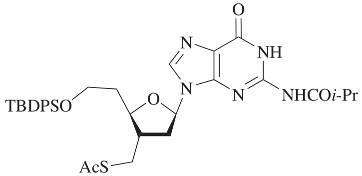
		Bu_3SnH, Et_3B, benzene, rt, 0.5 h		(70)	716
		Bu_3SnH, Et_3B, benzene, rt, 0.5 h		(73)[a]	716, 717
C_{12-17}		Bu_3SnH, AIBN, toluene, reflux, 1–2 h		Y H (43) NHc-C_5H_9 (24)[a]	718
		Bu_3SnH, AIBN, toluene, 80°, 5 h		Y R PhO H (93) MeO NH_2 (0)	719
		Bu_3SnH, AIBN, toluene, 75°, 3 h		(87)	34

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Bu_3SnH, AIBN, toluene, 100°, 2.5 h	 (38)	720
	Bu_3SnH, AIBN, toluene, 100°, 2 h	 (70)	720
	Bu_3SnH, AIBN, toluene, reflux	 R^1 R^2 DMTr BzO (—) TBDPS AcS (85)	687 94
	Bu_3SnH, AIBN, toluene, reflux	 (85–90)	94

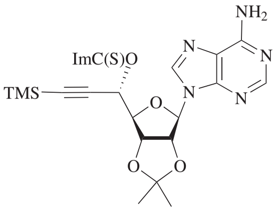
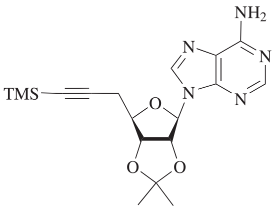
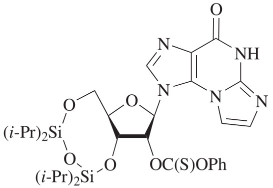
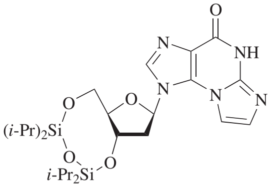
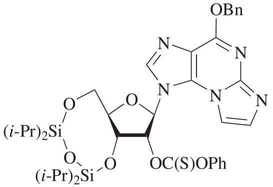
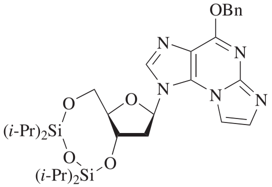
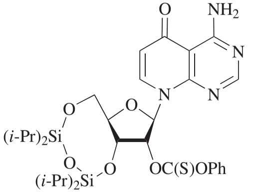
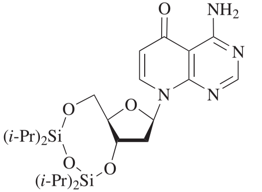
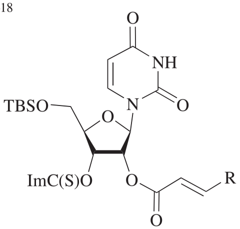
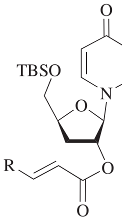
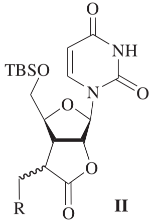
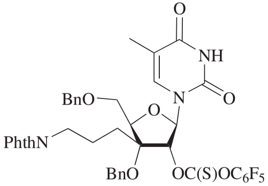
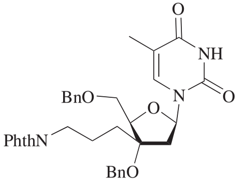
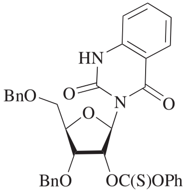
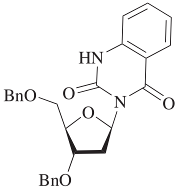
	Bu$_3$SnH, AIBN, toluene, 80°, 1 h		(53)^a	721
	Bu$_3$SnH, AIBN, toluene, reflux, 3 h		(65)	722
	Bu$_3$SnH, AIBN, toluene		(—)	722
	(TMS)$_3$SiH, ACCN, toluene, 105°, 15 h		(71)^b	723

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{13–18}$ 	Bu_3SnH (added over 24 h), benzene, reflux	 **I** +  **II** R I II Me (40) (42) Ph (29) (35)	711
C_{13} 	Bu_3SnH, AIBN, benzene, reflux, 1 h	 (25)	724
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (62)	725

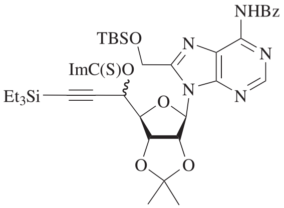
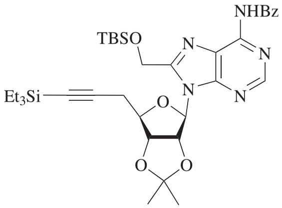
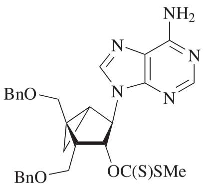
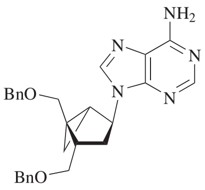
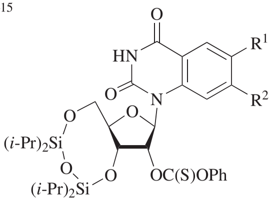
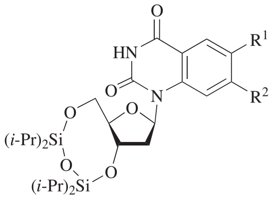
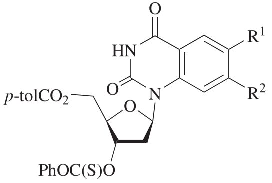
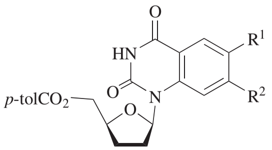
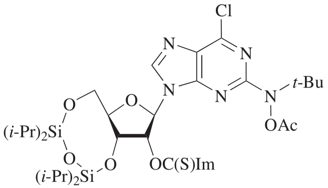
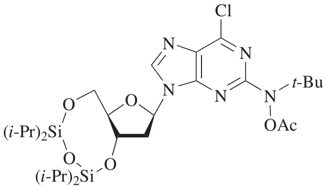
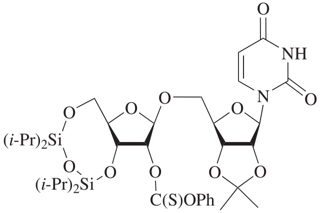
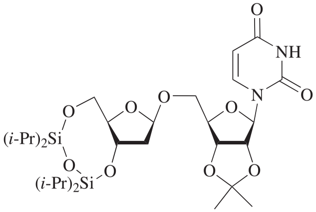
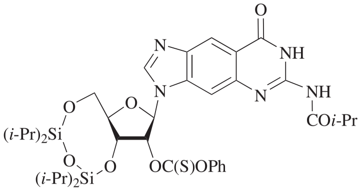
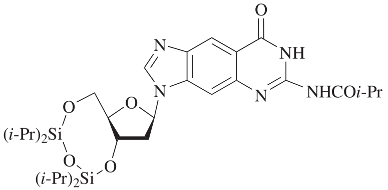
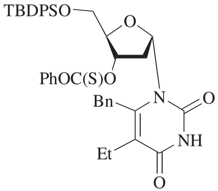
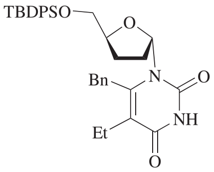
		Bu$_3$SnH, AIBN, toluene, 80°, 1.5 h	 (65)[a]	688
		Bu$_3$SnH, Et$_3$B, benzene, rt, 0.25 h	 (73)[a]	717, 716
C$_{13-15}$		Bu$_3$SnH, AIBN, toluene, 70°, 3 h	 R^1 R^2 H H (83) OMe OMe (74)[b] Me H (49)[b] H Me (60)[b] Me Me (62)[b]	726
		Bu$_3$SnH, AIBN, toluene, 75°, 3 h	 R^1 R^2 H H (99)[a] Me H (72)[a] H Me (81)[a] Me Me (89)[a]	726

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	Bu_3SnH, AIBN, toluene, reflux	 (96)	727
	Bu_3SnH, AIBN, toluene, 80°, 3 h	 (92)	728
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (71)	729
C_{18}			
	Bu_3SnH, AIBN, toluene	 (7)[b]	730

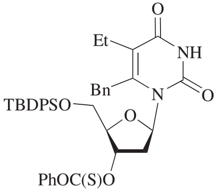
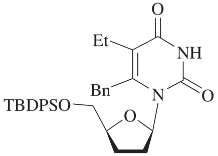
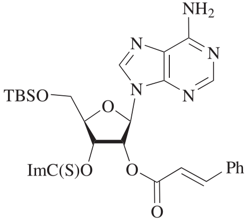
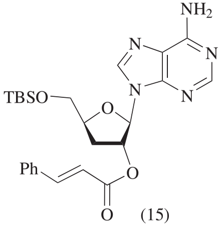
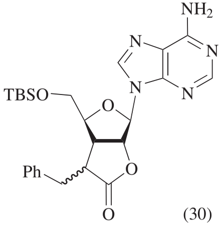
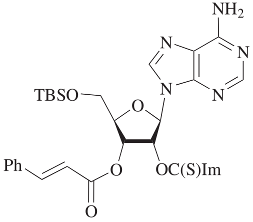
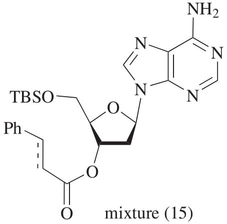
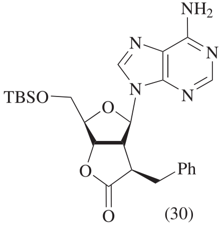
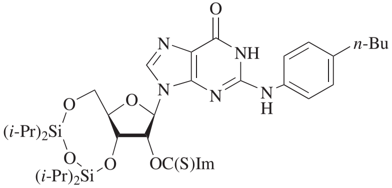
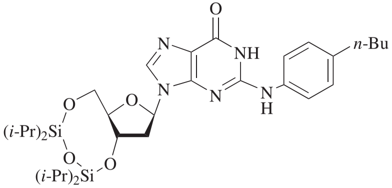
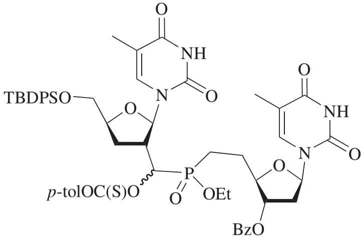
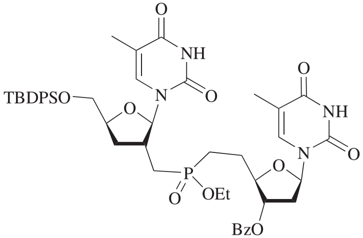
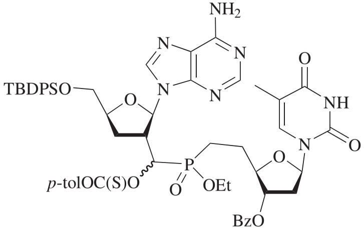
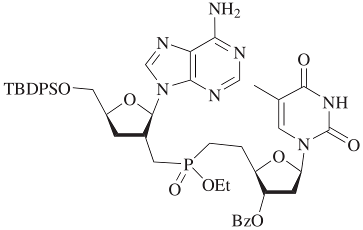
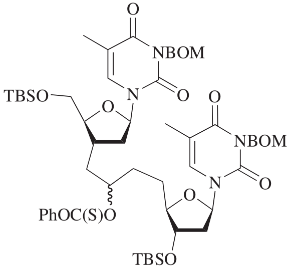
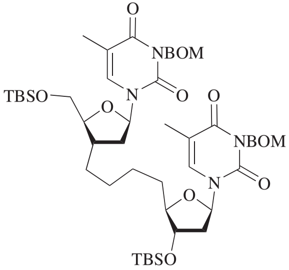
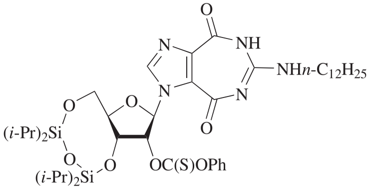
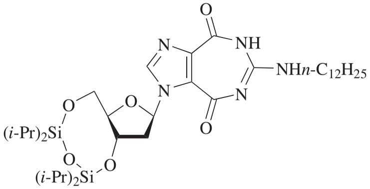
		Bu_3SnH, AIBN, toluene	 (10)[b]	730
C₁₉		Bu_3SnH (added over 24 h), benzene, reflux	 (15) +  (30)	711
		Bu_3SnH (added over 24 h), benzene, reflux	 mixture (15) +  (30)	711
C₁₀		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (92)	731

TABLE 2B. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	Bu_3SnH, AIBN, toluene, 80°, 20 h	 (55)[a]	732
	Bu_3SnH, AIBN, toluene, 80°, 20 h	 (27)[a]	732
C_{23} 	Bu_3SnH, AIBN, toluene, reflux	 (—)	733

C_{11}		Bu_3SnH, AIBN, toluene, reflux, 24 h	 (77)	734

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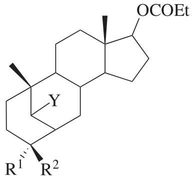
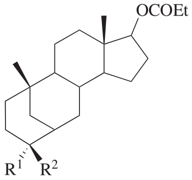
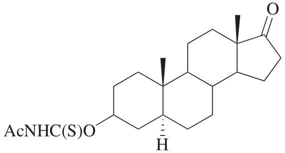
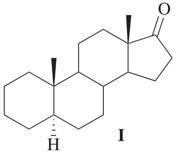
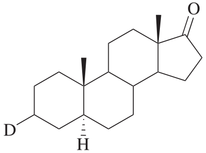
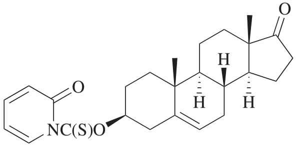
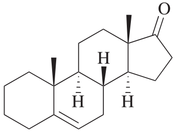
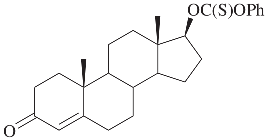
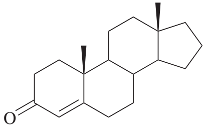
[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	Bu_3SnH, toluene, reflux	 R^1 R^2 Y AcO H OC(S)Ph (69) AcO H OC(S)Im (—) =O OC(S)Ph (55) =O OC(S)Im (83)	735
C_{19} 	Bu_3SnH, AIBN, benzene, reflux, 1 h	 **I** (95)	77
	Ph_3SiH, Et_3B, O_2, benzene, rt, 10 min	**I** (67)	77
	Bu_3SnD, AIBN, benzene, reflux, 0.5 h	 (98)	77
	Bu_3SnH, AIBN, toluene, reflux, 1–2 h	 (78)[a]	74
C_{19} 	Polystyrene-linked Bu_2SnH, AIBN, toluene, 80°	 (98)	104

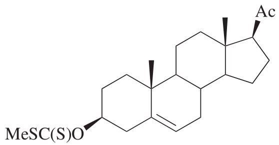
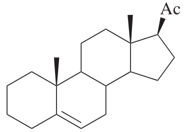
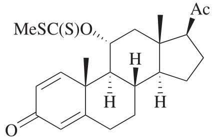
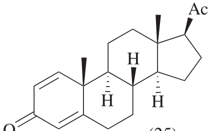
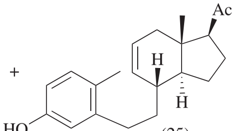
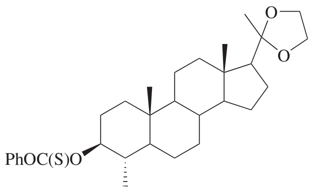
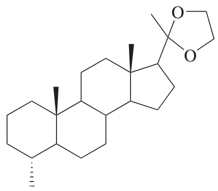
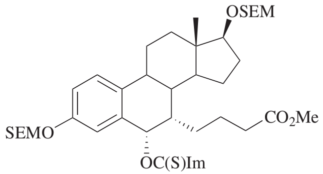
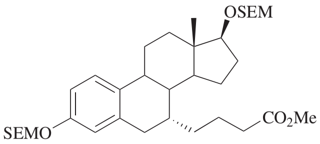
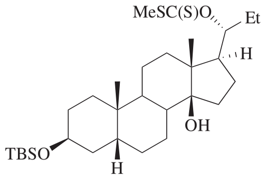
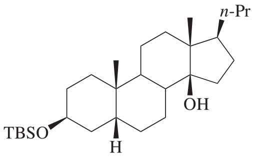
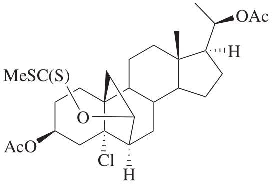
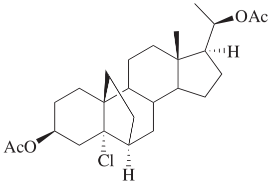
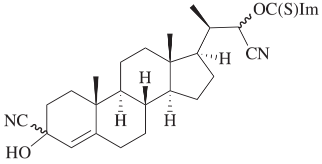
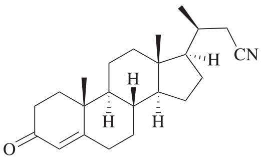
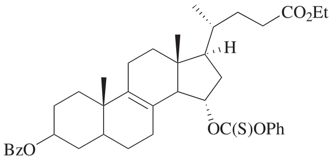
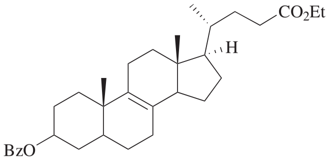
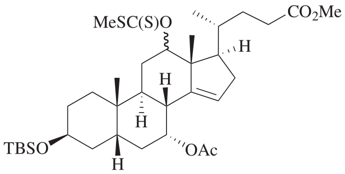
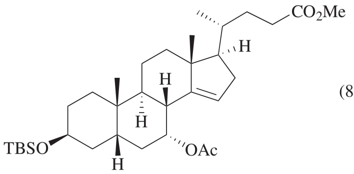
		Bu_3SnH, AIBN, toluene, reflux, 4 h	 (84)	105
C_{21}		Bu_3SnH, AIBN, toluene, reflux, 40 h	 (25) +  (25)	736, 60
C_{22}		Bu_3SnH, AIBN, benzene, reflux, 7.5 h	 (82)	737, 738
		Bu_3SnH, AIBN, toluene, 80°, 4 h	 (95)	739
		$(TMS)_3SiH$, AIBN, toluene, reflux, 3 h	 (83)^a	740

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
	Ph_2SiH_2, AIBN, toluene, 90°, 5.5 h	 $(37)^b$	741
C_{23}			
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 0.5 h	 $(85)^b$	27
C_{24}			
	Bu_3SnH, AIBN, toluene, 90°, 1 h	 (75)	742
	Bu_3SnH, AIBN, toluene, reflux	 (86)	743

C_{27}

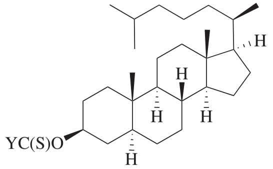
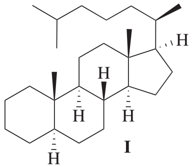
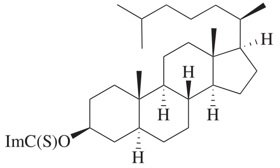
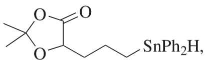
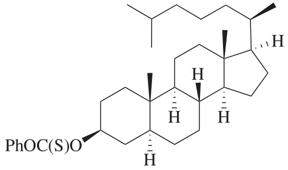
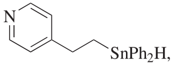
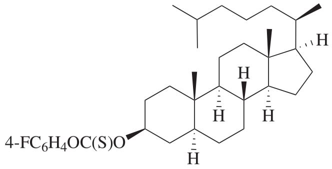
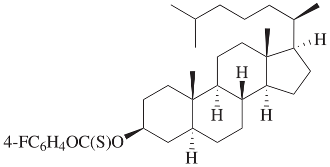
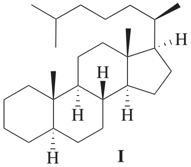
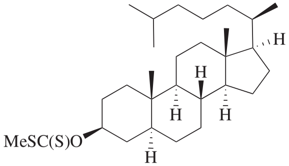
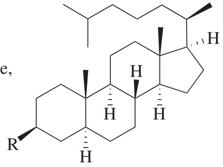
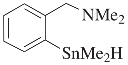
	Bu_3SnH, solvent	 **I** Y Solvent Temp (°) H toluene 110 (9) H xylene 140 (24) Ph toluene reflux (73) Im toluene reflux (73)	 33 33 1 1
	 $SnPh_2H$, AIBN, toluene, reflux, 10 h	**I** (91)	164
	$Ph_2SiHSiHPh_2$ (1.1 eq), AIBN (0.3 eq), EtOAc, reflux, 16 h	**I** (92)	186
	Ph_2SiH_2, Et_3B, O_2, benzene, reflux, 0.5 h	**I** (93)	173
	 $SnPh_2H$, AIBN, toluene, reflux	**I** (90)	165
	Ph_2SiH_2, Et_3B, O_2, benzene, reflux, 0.5 h	**I** (93)	173
	$PhSiH_3$, Bz_2O_2, toluene, reflux, 80 min	**I** (87)	172

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27}		Et_3SiH (neat), Bz_2O_2 (0.6 eq), reflux, 1.5 h	 **I** (93)	367
		$(MeO)_2P(O)H$, Bz_2O_2, dioxane, reflux, 2 h	**I** (91)	112, 194
		H_3PO_2 (5 eq), Et_3N (5.5 eq), dioxane, reflux, 2.5 h	**I** (93)	112, 194
		Bu_3SnH (3 eq), AIBN, benzene, reflux, 3 h	 R — H (39) R — $HSCH_2O$ (—)	20
		 $SnMe_2H$ (2 eq), AIBN, benzene, reflux, 0.5 h	**I** (75)	166
		Et_3SiH (*x* eq), dicumyl peroxide (0.05 eq), *t*-$C_{12}H_{25}SH$ (*y* eq), octane, reflux	**I** *x* / *y* / Time (h) / **I** 2 / 0 / 2 / (49) 2 / 0.02 / 2 / (72) 4 / 0.02 / 4 / (89)	175, 170
		Ph_3SiH (1.5 eq), TBHN, dioxane, 60°	**I** (85)	176
		Ph_3SiH, $(t\text{-}BuOO)_2CMe_2$, octane, reflux	**I** (85)	176

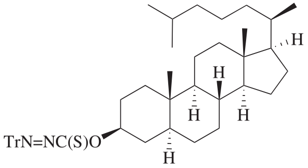
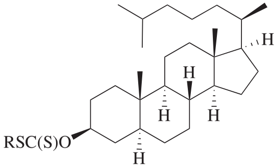
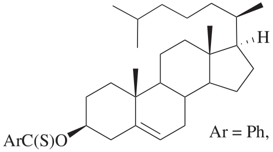
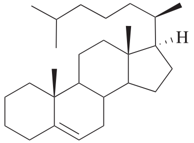
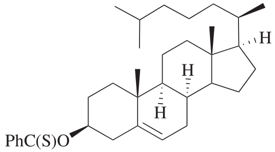
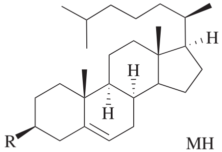
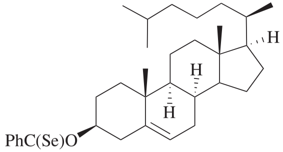
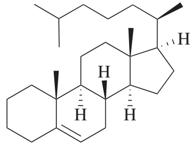
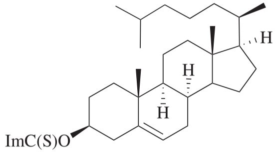
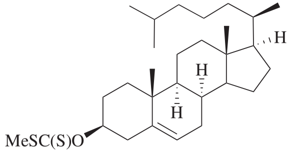
	$R_2SiHSiHR_2$ (1.1 eq), AIBN (0.3 eq), EtOAc, reflux, 16 h	**I** R / **I** Ph (89) 4-FC_6H_4 (81)	186
	$R_2P(O)H$, $(t\text{-}Bu)_2O_2$, dioxane, reflux	**I** R / Time (h) / **I** *n*-Bu 16 (97) Ph 32 (95)	205 206
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), DMF, 40°, 1 h	**I** (96)	211
	$(TMS)_3CH$ (2 eq), AIBN (3 eq), benzene, 80°, 12 h	**I** (86)	210
	*t*-BuSH, toluene, reflux, 1 h	**I** (49)	20
	Bu_3SnH, AIBN, solvent, reflux	**I** R / Solvent / **I** *i*-Pr C_6D_6 (67) Ph toluene (—) 2,4,6-$Me_3C_6H_2$ toluene (—) Bu_3Sn toluene (—)	19, 20
 Ar = Ph, 4-$MeOC_6H_4$, 4-$MeSO_2C_6H_4$, 2,4-$(MeO)_2C_6H_3$	Bu_3SnH (1.5 eq), ia, toluene, reflux	 ("good")	1

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27}		MH (*x* eq), AIBN (cat.), toluene, reflux	 **I** R = H **II** R = OH **III** R = OBn MH / *x* / **I** / **II** / **III** Bu_3SnH / 1.5 / (46) / (42) / (—) Bu_3SnH / 5 / (0) / (38) / (49) Ph_3SnH / 5 / (trace) / (trace) / (97)	15
		Bu_3SnH (1.5 eq), toluene, reflux	 (60)	1
		Bu_3SnH (1.5 eq), toluene, reflux	**I** (74)	1
		Bu_3GeH, ACCN, MeCN, ia, reflux, 3 h	**I** (67)	189
		Bu_3SnH (1.5 eq), toluene, reflux	**I** (78)	1
		Polystyrene-linked Bu_2SnH, AIBN, toluene, 80°	**I** (80)	104

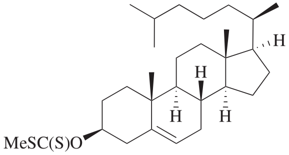
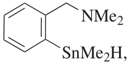
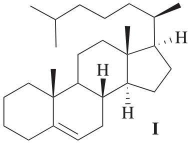
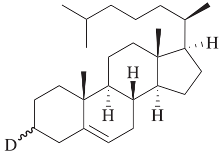
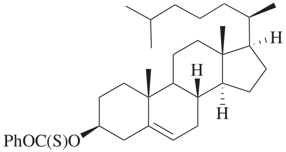
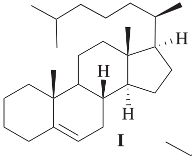
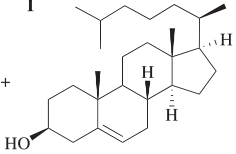
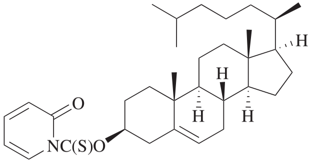
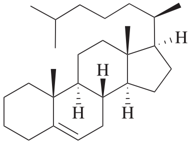
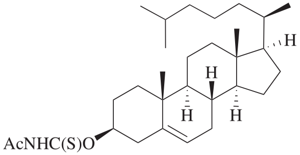
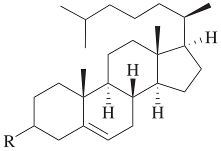
	 $SnMe_2H$, AIBN, benzene, reflux, 0.5 h	**I** (75)	166
	Et_3SiH, dicumyl peroxide, $t\text{-}C_{12}H_{25}SH$ (x eq), reflux	**I** Solvent / x / Time (h) / **I** octane / 0 / 2 / (49) octane / 0.02 / 2 / (72) decane / 0.02 / 2 / (89)	175
	EPHP, ACVA, CTAB, H_2O, 80°, 12 h	**I** (28)	199
	EPHP, Et_3B, O_2, CTAB, EtOH, rt, 1 h	**I** (91)	199
	$n\text{-}C_{16}H_{33}NMe_3^+\ H_2PO_2^-$, ACVA, H_2O, reflux, 12 h	 **I** (7)	201
	Me_3B (5 eq), H_2O (5 eq), O_2 (0.8 eq as air, added slowly), benzene, rt	**I** (71)	38
	R_3B (5 eq), D_2O (x eq), O_2 (0.8 eq as air, added slowly), benzene, rt	 R / x Me / 20 / (67) Bu / 5 / (19)	38

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{27}$ 	Bu_3SnH, $(t\text{-}Bu)_2O_2$, toluene, reflux, 4 h	 **I** (84)	34
	Bu_3SnH, xylene, reflux, 4 h	**I** (minor) +  (major)	34
	Polystyrene-linked Bu_2SnH, AIBN, toluene, 80°	**I** (72)	104
	$(TMS)_3SiH$, AIBN, toluene, 80°, 2 h	**I** (94)	90
	$PhSiH_3$, Bz_2O_2, toluene, reflux, 1.25 h	**I** (87)	367
	Et_3SiH (neat), Bz_2O_2, reflux, 1.5 h	**I** (93)	367
	Bu_3SnH, AIBN, toluene, reflux, 1–2 h	 (83)[a]	74
	Bu_3SnR, benzene, reflux, 20 min	 R: H (60); D (74)	77

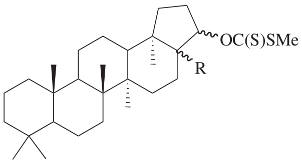
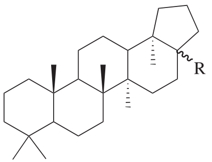
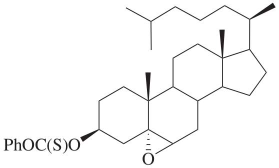
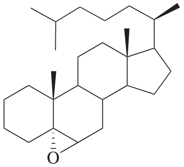
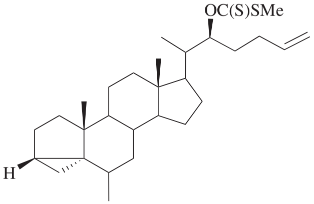
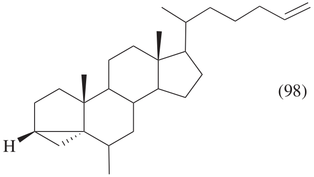
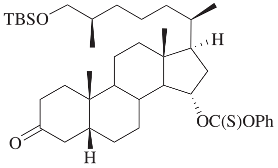
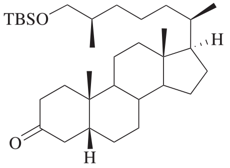
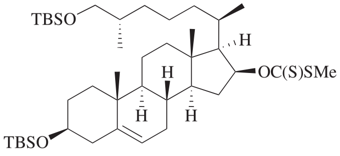
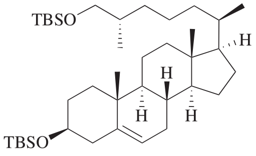
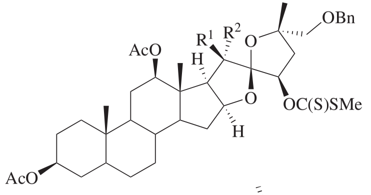
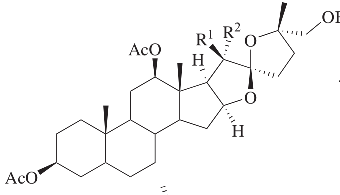
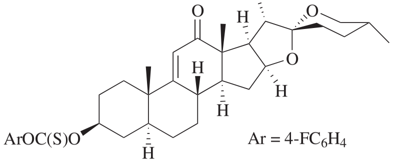
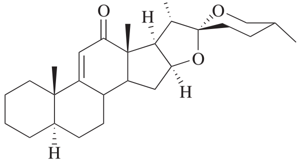
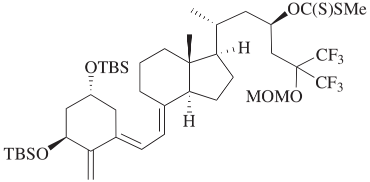
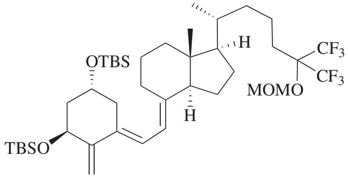
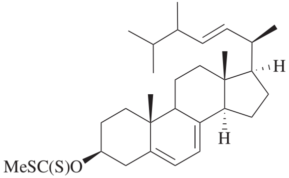
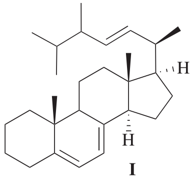
	Bu_3SnH, toluene		R α-H (50) β-H (67)	744
	Bu_3SnH, $(t\text{-}Bu)_2O_2$, toluene, reflux, 3 h		(78)	34
	Bu_3SnH, toluene		(98)	745
	Bu_3SnH, AIBN, toluene, reflux, 12 h		(82)	103
	Bu_3SnH, AIBN, toluene, reflux, 18 h		(75)[a]	266

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27} 	Bu_3SnH, toluene, reflux, 0.5 h	 R^1 R^2 H Me (81) Me H (88)	746
 Ar = 4-FC_6H_4	MH, initiator, solvent		

MH	Initiator	Solvent	Temp	Time (h)		Refs.
Ph_2SiH_2	Et_3B	benzene	rt	0.5	(83)	173
Ph_3SiH	Bz_2O_2	toluene	reflux	3.75	(83)	367
$PhSiH_3$	AIBN	toluene	reflux	1.5	(85)	367

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu_3SnH, toluene, reflux, 1 h	 (97)	100
C_{28} 	Bu_3SnH, toluene, reflux	 **I** (67)	1

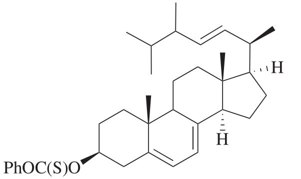
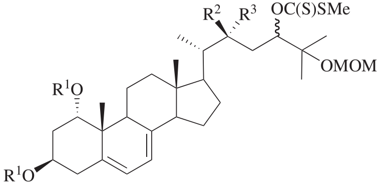
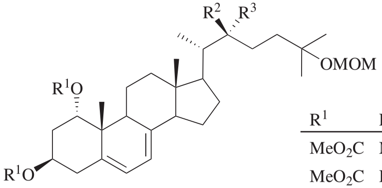
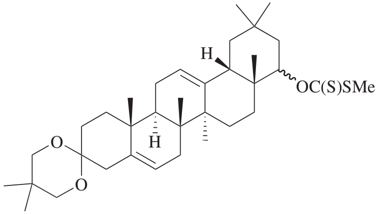
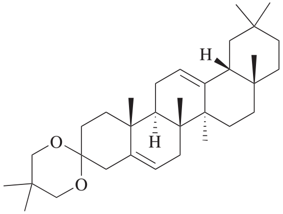
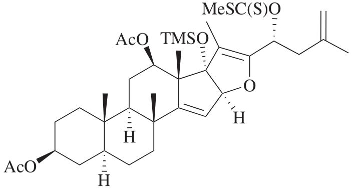
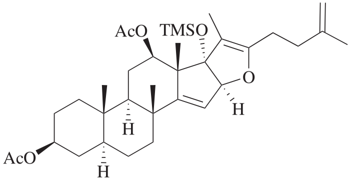
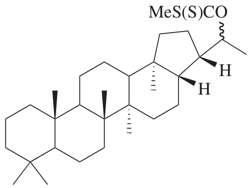
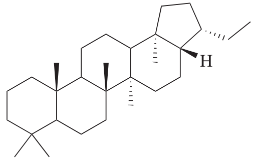
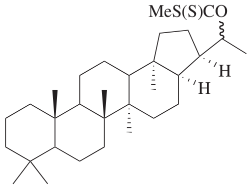
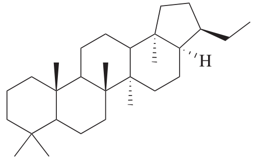
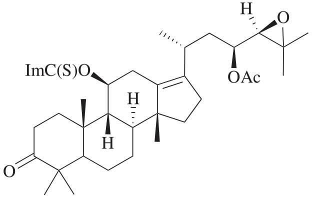
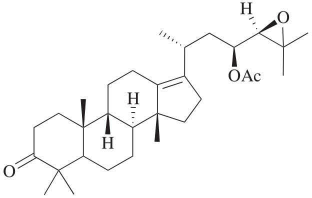
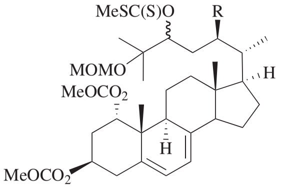
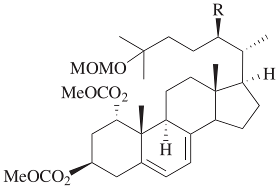
	Polystyrene-linked Bu$_2$SnH, AIBN, toluene, 80°	**I** (65)	104
	Bu$_3$SnH, AIBN, toluene, reflux, 0.25 h	 R^1 R^2 R^3 MeO$_2$C Me H (90) MeO$_2$C H Me (85)	747
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h	 (95)	748
	Ph$_3$SnH, AIBN, toluene, reflux, 5 min	 (90)	749

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29}		Bu_3SnH, toluene, reflux	 (46)	750
		Bu_3SnH, toluene, reflux	 (52)	750
		Bu_3SnH, AIBN, toluene, reflux, 5 min	 (—)	747
$C_{29–31}$		Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 R Et (90) Bu (89)	751

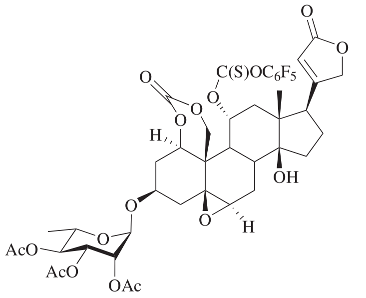
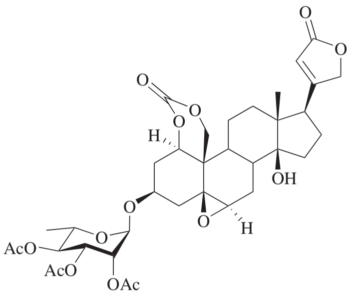
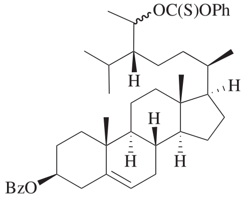
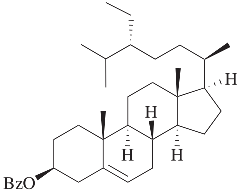
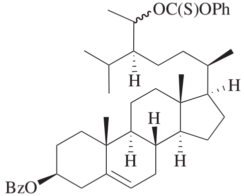
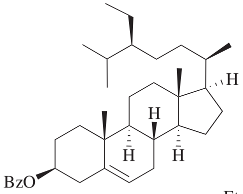
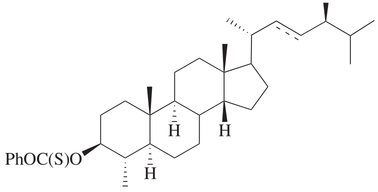
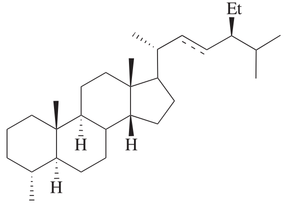
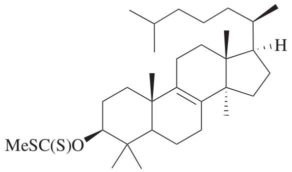
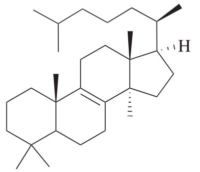
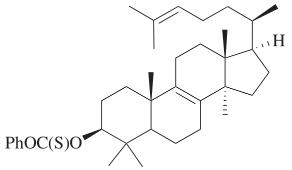
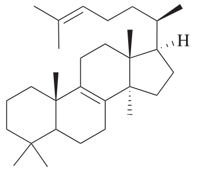
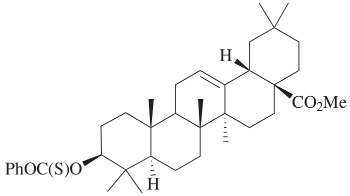
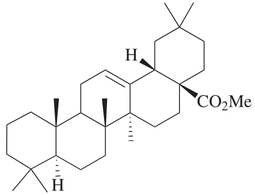
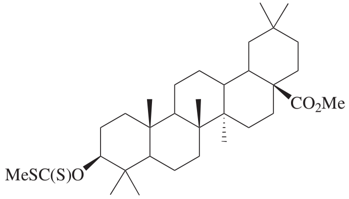
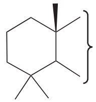
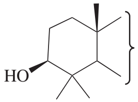
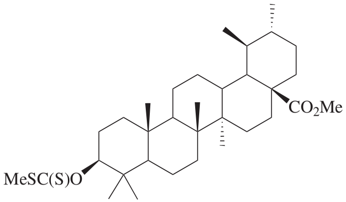
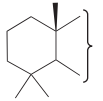
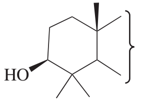
C_{29} 	Bu_3SnH, benzene, reflux		(100)	752
	Bu_3SnH		(—)	753
	Bu_3SnH		(—)	753
C_{30} 	Bu_3SnH, AIBN, benzene, reflux, 7.5 h		Bond double (81) single (83)	738

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30}		Bu_3SnH, xylene, reflux, 2.5 h	 (83)	1
		$(TMS)_3SiH$, AIBN, toluene, 80°, 2 h	 (80)	90
		PMHS, $(Bu_3Sn)_2O$ (cat.), AIBN, toluene, 80°, 24 h	 (90)	242
		$h\nu$, MH, solvent, rt	 **I** +  **II** + SM	291

MH	Solvent	Time (h)	**I**	**II**	SM
$(EtO)_2P(O)H$	HMPA	1.5	(44)	(2)	(54)
$(EtO)_2P(O)H$	benzene	8	(13)	(11)	(54)

	*h*ν, MH, sensitizer, solvent, rt	 **I** +  **II** + SM	291

MH	Sensitizer	Solvent	Time (h)	**I**	**II**	SM
$(EtO)_2P(O)H$	none	HMPA	1.5	(40)	(34)	(26)
$(EtO)_2P(O)H$	none	benzene	8	(22)	(9)	(69)
$(EtO)_2P(O)H$	none	dioxane	8	(7)	(42)	(51)
$(EtO)_2P(O)H$	Ph_2CO	dioxane	8	(46)	(36)	(18)

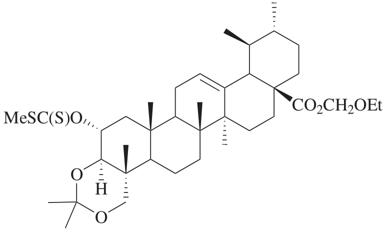
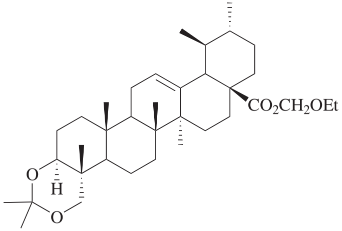
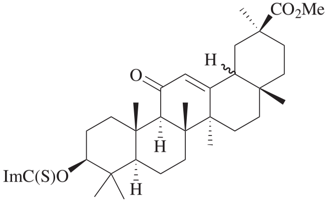
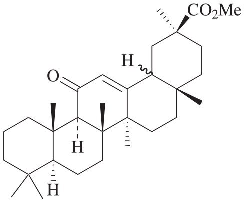
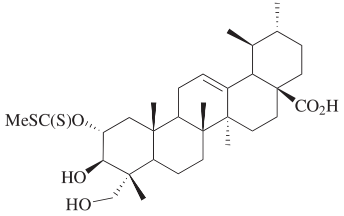
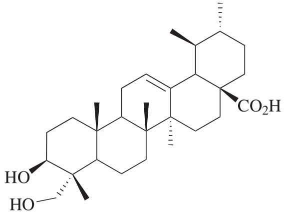
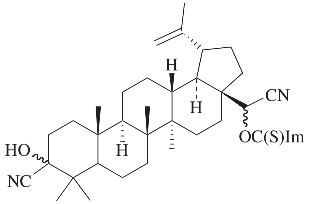
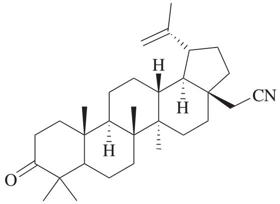
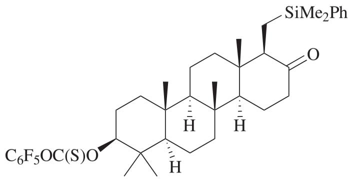
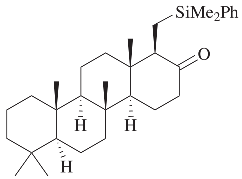
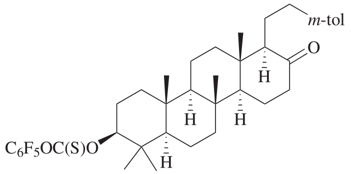
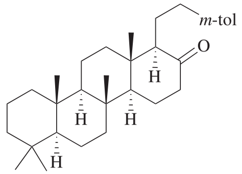
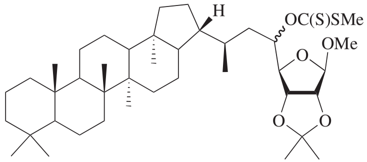
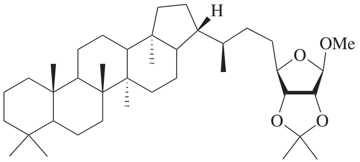
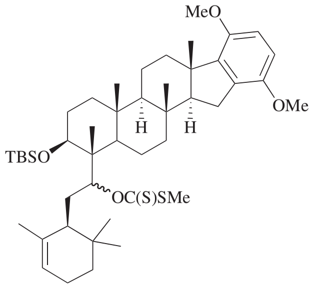
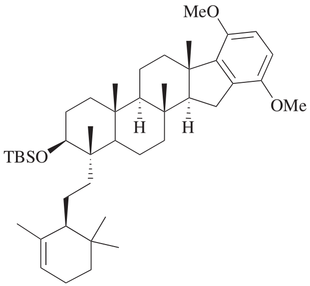
	Bu_3SnH, toluene, reflux, 2 h	 (85)	412
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 (68)[a]	754

TABLE 2C. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30}		$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), DMF, 50°, 4 h	 (95)	211
C_{31}		Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 30 min	 (78)[b]	27
C_{32}		Bu_3SnH, AIBN, benzene, reflux, 3 h	 (94)	755
		Bu_3SnH, AIBN, benzene, reflux, 4 h	 (90)[a]	756

C_{35}		Bu_3SnH, AIBN, toluene, 80°, o/n		(98)	757
C_{36}		Bu_3SnH (neat), AIBN, 80°		(78)[a]	245

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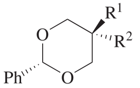
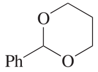
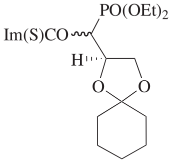
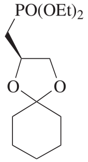
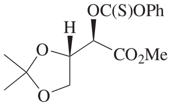
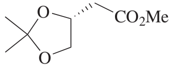
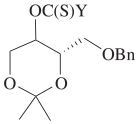
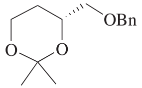
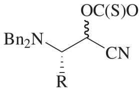
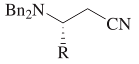
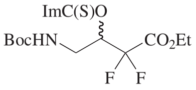
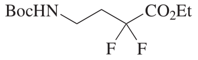
[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3	 R^1 R^2 OC(S)SMe H H OC(S)SMe	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (—)	30
		Bu_3SnH, toluene, reflux, 2.5 h	 $(65)^a$	535
C_4		Bu_3SnH, AIBN, toluene, 80°, 50 min	 (90)	758
		MH, AIBN, additive, toluene, reflux		155
		Y MH Additive Time (h) SMe Bu_3SnH — o/n (89) SMe PMHS + $(Bu_3Sn)_2O$ BuOH >36 (31) OPh PMHS + $(Bu_3Sn)_2O$ BuOH >36 (31) Im Bu_3SnH — o/n (49)		
C_{4-9}	 R = Me, *i*-Pr, Ph	Bu_3SnH, AIBN	 (57–67)	759
		Et_3SiH, Bz_2O_2, toluene, reflux, 2 h	 $(84)^b$	760

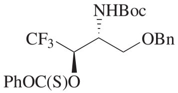
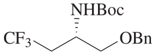
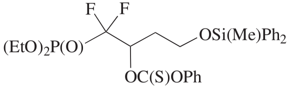
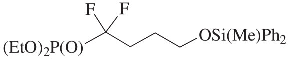
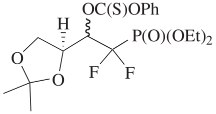
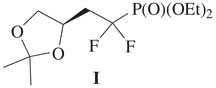
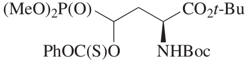
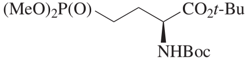
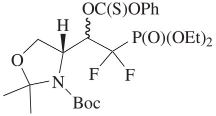
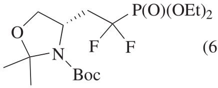
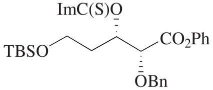
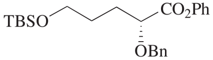
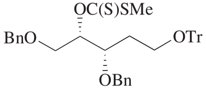
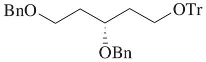
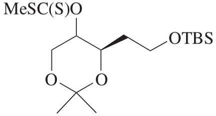
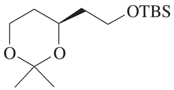
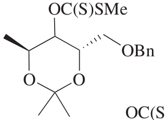
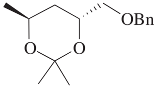
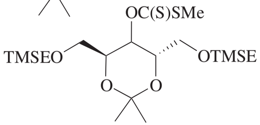
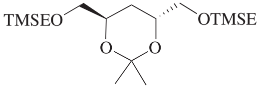
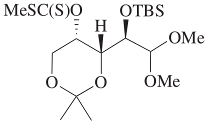
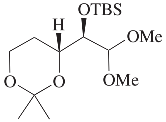
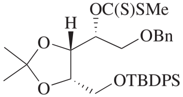
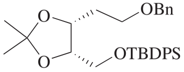
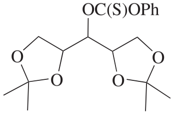
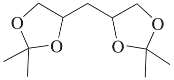
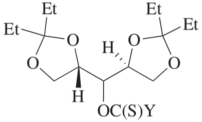
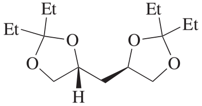
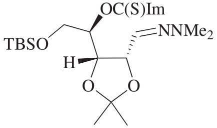
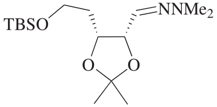
C_4		Bu_3SnH, AIBN, toluene, 80°, 1 h		(85)	761
		Bu_3SnH, AIBN, toluene, reflux, 2 h		(86)	472
		Bu_3SnH, AIBN, toluene, reflux, 2 h	 **I**	(66)	762
		Bu_3SnH, AIBN, toluene, reflux, 2 h	**I** (82)		472
		$(TMS)_3SiH$, toluene, 80°, 2 h		(95)	763
		Bu_3SnH, AIBN, toluene, reflux, 2 h		(68)	764
C_5		Bu_3SnH, toluene, reflux		(86)	765
		Bu_3SnH, AIBN, toluene, reflux, 18 h		$(54)^b$	766
		Bu_3SnH, AIBN, toluene, reflux, 20 h		(82)	767

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	Polystyrene-linked Bu_2SnH, AIBN, benzene, reflux, 20 h	 (78)	155
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (98)	155
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (94)	768
	Bu_3SnH, toluene, reflux	 (46)[a]	769
	Bu_3SnH, AIBN, benzene, 75°, 8 h	 (87)	770
	MH, initiator, toluene, reflux, 3.5 h	 Y — MH — Initiator SMe — Bu_3SnH — AIBN (89) SMe — Et_3SiH — Bz_2O_2 (97) Im — Et_3SiH — Bz_2O_2 (93)	771
	Bu_3SnH, benzene, reflux	 (41)	23

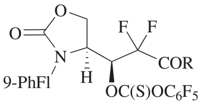
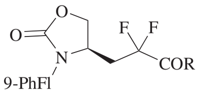
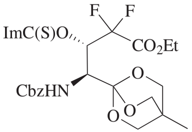
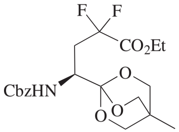
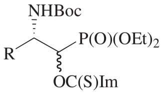
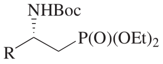
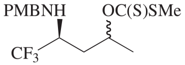
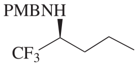
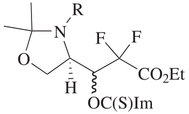
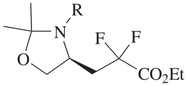
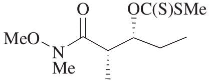
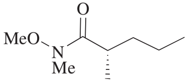
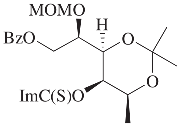
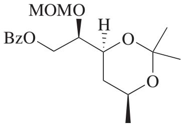
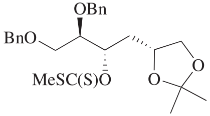
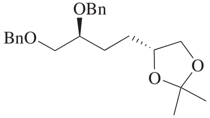
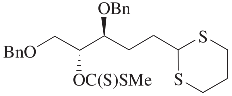
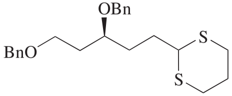
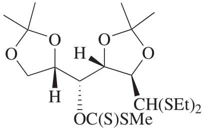
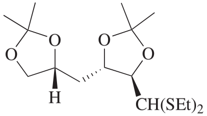
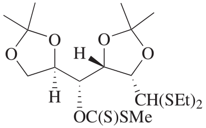
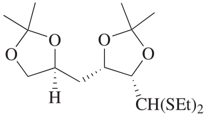
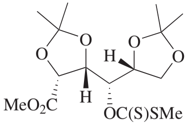
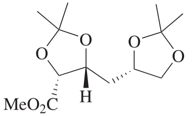
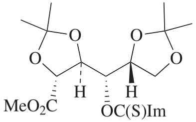
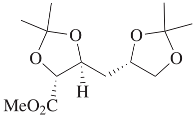
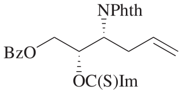
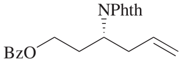
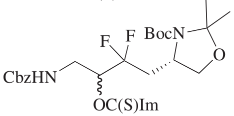
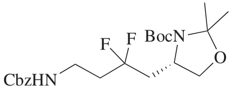
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 R OEt (39) NMe_2 (49)	772
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (83)	772
$C_{5–9}$			
	Et_3SiH, Bz_2O_2, reflux, 1 h	 R *i*-Pr $(74)^b$ $PhCH_2$ $(76)^b$ 4-(*t*-BuO)$C_6H_4CH_2$ $(70)^b$	773
C_5			
	Bu_3SnH, Et_3B, benzene, rt	 (67)	774
	Et_3SiH, Bz_2O_2, reflux	 R Boc (100) Cbz (62)	775 776
C_6			
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (96)	777
	Bu_3SnH, toluene, reflux, 8 h	 (55)	778
	Bu_3SnH, toluene, reflux, 18 h	 (75)	779

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	Bu_3SnH, AIBN, toluene, reflux, 18 h	 (96)	780
	Bu_3SnH, toluene, reflux, 16 h	 (—)	597
	Bu_3SnH, toluene, reflux, 16 h	 $(85)^b$	781
	Bu_3SnH, toluene, reflux, 19 h	 (85)	782
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 $(65)^b$	783
	Bu_3SnH, AIBN, toluene, reflux, 16 h	 (82)	784
	Et_3SiH, Bz_2O_2, toluene, reflux, 2 h	 (71)	760

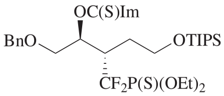
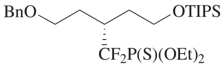
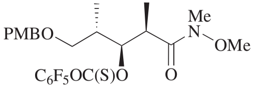
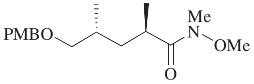
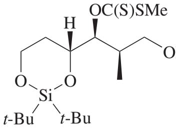
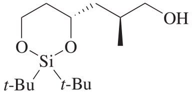
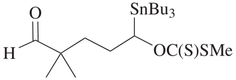
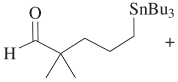
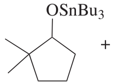
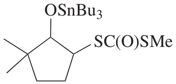
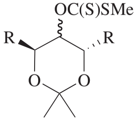
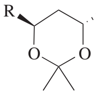
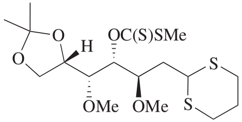
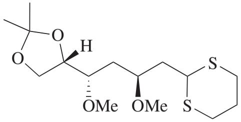
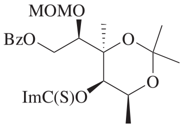
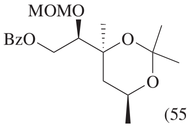
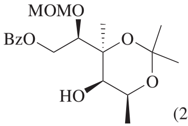
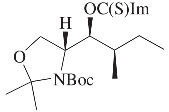
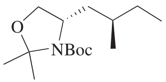
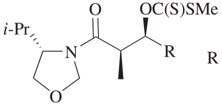
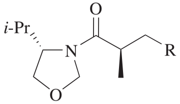
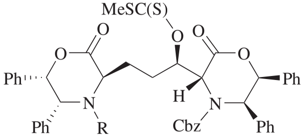
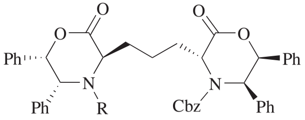
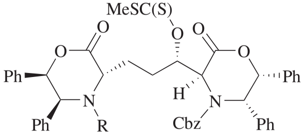
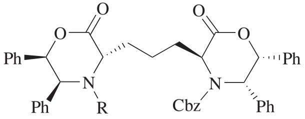
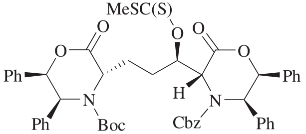
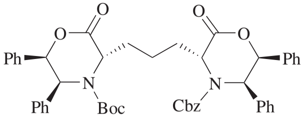
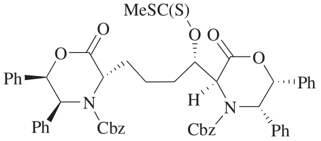
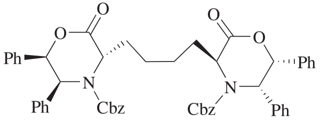
C$_6$		Bu$_3$SnH, AIBN	 (91)	785
C$_7$		Bu$_3$SnH, AIBN	 (—)	786
		Bu$_3$SnH, AIBN, toluene, reflux	 (97)	787
		Bu$_3$SnH, AIBN, benzene, reflux	 (7) +  (48) +  (9)	788
C$_{7-9}$		Polystyrene-linked Bu$_2$SnH, AIBN, benzene, reflux, 20 h	 R Et (53) *i*-Pr (89)	155
C$_7$		Bu$_3$SnH, AIBN, toluene, reflux, 14 h	 (81)	789
		Bu$_3$SnH, toluene, reflux	 (55) +  (27)	778

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	H_3PO_2, Et_3N, AIBN, dioxane, reflux	 $(72)^b$	790
C_{7-8}  R = *i*-Pr, *n*-Bu	Bu_3SnH, toluene, reflux	 (—)	791
C_7 	Ph_3SnH, AIBN, toluene, reflux	 R Cbz (73) Boc (79)	792
	Ph_3SnH, AIBN, toluene, reflux	 R Cbz (62) Boc (83)	792
	Ph_3SnH, AIBN, toluene, reflux	 (83)	792
C_8 	Ph_3SnH, AIBN, toluene, reflux	 (57)	792

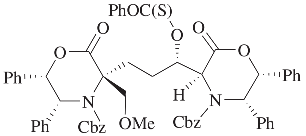
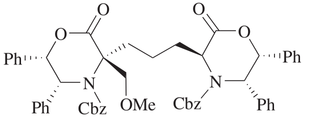
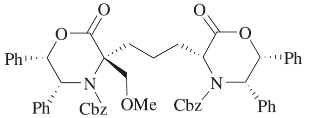
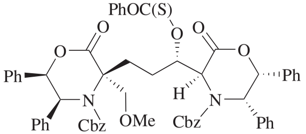
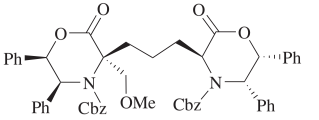
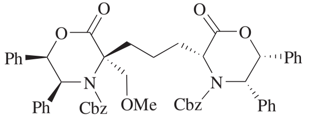
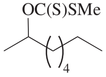
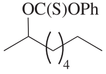
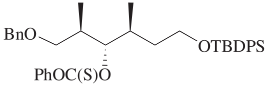
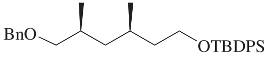
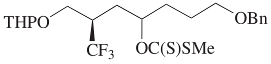
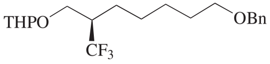
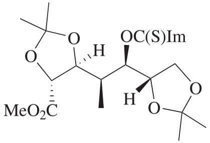
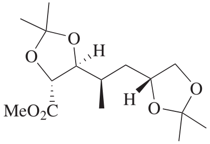
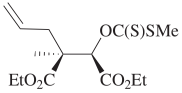
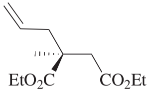
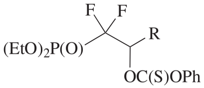
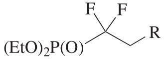
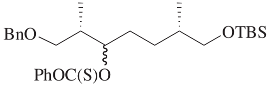
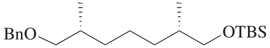
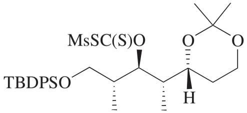
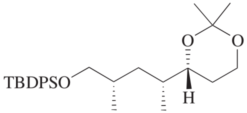
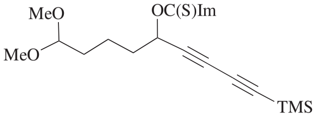
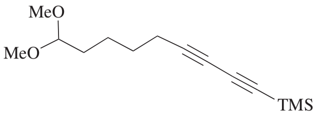
C_8			
	Ph_3SnH, toluene, reflux	 (49) +  (11)	158
	Ph_3SnH, toluene, reflux	 (81) +  (5)	158
	Et_3SiH (2 eq), t-$C_{12}H_{25}SH$ (x eq), 1,1-di-(*tert*-butylperoxy)- cyclohexane (0.02 eq), cyclohexane, sealed tube, 115°, 1 h	 x 0 (63)^c 0.02 (92)^c	175 170
	Polystyrene-linked- Bu_2SnH (cat.), AIBN, $(MeO)_3SiH$ (15 eq), n-BuOH (16.5 eq), toluene, reflux, 24 h	 (70)^c	156
	Bu_3SnH (neat), AIBN, 100°, 20 min	 (68)	793

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	Bu_3SnH, AIBN, toluene, 80°, o/n	 (70)	794
	Et_3SiH, Bz_2O_2, reflux, 40 min	 (78)	795, 796
	Bu_3SnH, toluene, reflux	 (—)	797
C_9			
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 R Ph (89) c-C_6H_{11} (84) n-C_6H_{13} (81)	472
	Bu_3SnH, AIBN	 (90)	798
	Bu_3SnH, AIBN, toluene, 100°	 (90)^b	799
	Bu_3SnH, AIBN, toluene, 80°, 1 h	 (51)^b	102

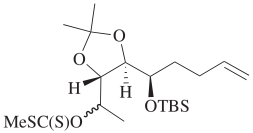
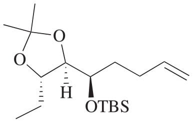
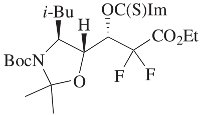
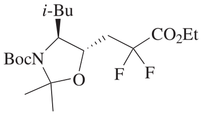
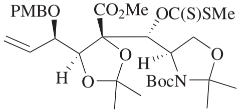
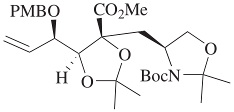
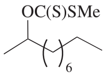
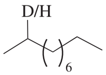
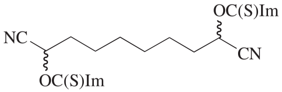
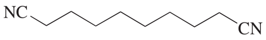
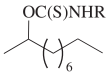
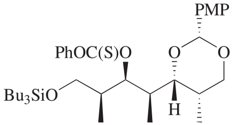
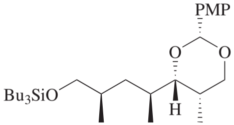
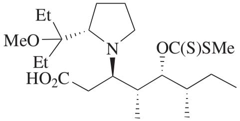
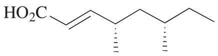
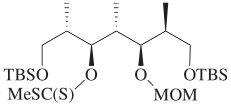
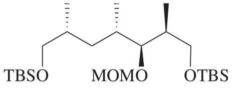
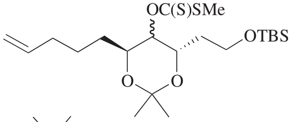
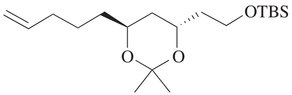
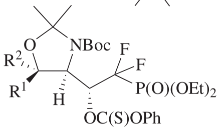
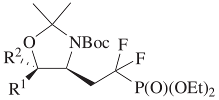
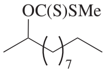
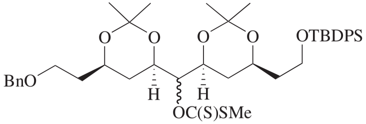
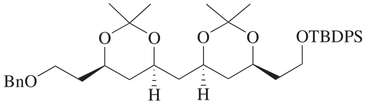
	Bu$_3$SnH, AIBN, benzene, reflux, 4 h		(55)[a]	800
	Et$_3$SiH, Bz$_2$O$_2$		(78)	801
	Bu$_3$SnH, AIBN, toluene, reflux		(53)[b]	802, 803
C$_{10}$				
	Et$_3$B (5 eq), H$_2$O (x eq), O$_2$, benzene, rt, 6 h		x 0 (83)[c] 5 (73)[c]	215
	Et$_3$B (x eq), D$_2$O (5 eq), pyridine (y eq), O$_2$, benzene, rt, 6 h		x y % D 10 0 (82)[c] 53 5 0 (71)[c] 80 5 1 (—) 74 5 3 (61)[c] 62 5 5 (50)[c] 33 5 10 (24)[c] 1	215
	Bu$_3$SnH, AIBN, CH$_2$Cl$_2$, sunlamp, 20°, 30 min		(82)[a]	27
	Et$_3$SiH, (t-Bu)$_2$O$_2$ or Bz$_2$O$_2$, benzene, 140°, sealed tube		R Isolated GC Et (42) (90) Ph (52) (81) Bn (1) (—) CH$_2$TMS (85) (90)	75

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Bu_3SnH, AIBN, benzene, reflux, 30 min	 (81)	804
	Bu_3SnH, AIBN, toluene, sealed bomb, 165°, 1.5 d	 (65)	805
	Bu_3SnH, AIBN, benzene, reflux	 (85)[a]	806
	Bu_3SnH, AIBN, toluene, reflux	 (91)[a]	807
	Bu_3SnH, AIBN, toluene, 90°, 2 h	 R^1 R^2 Ph H (55)[b] H Ph (—)[b]	808
C_{11}			
	EPHP (5 eq), ACVA (0.75 eq), CTAB (2 eq), H_2O, 80°, 9 h	 (88)	199
	Bu_3SnH, AIBN, toluene, reflux	 (90)[a]	809

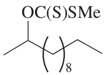
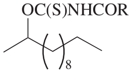
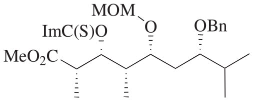
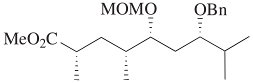
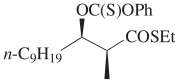
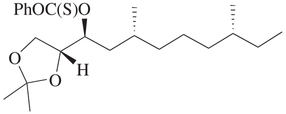
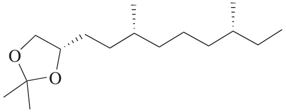
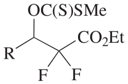
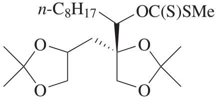
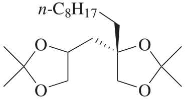
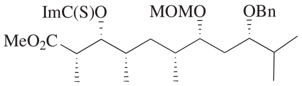
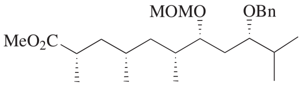
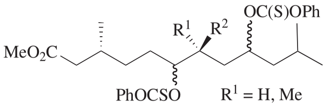
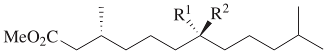
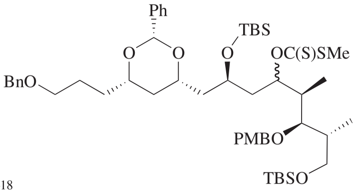
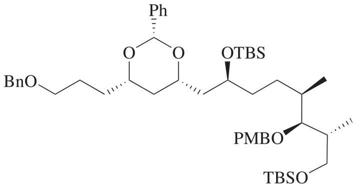
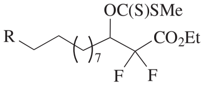
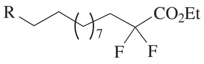
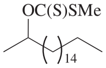
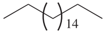
<table>
<tr><td colspan="4">C_{12}</td></tr>
<tr><td></td><td>n-$C_{16}H_{33}NMe_3^+\ H_2PO_2^-$ (3 eq), ACVA (0.5 eq), H_2O, reflux, 5 h</td><td>
I (90)</td><td>201</td></tr>
<tr><td></td><td>$R_2P(O)H$, initiator, dioxane, reflux, 24 h</td><td>I<table><tr><th>R</th><th>Initiator</th><th>I</th></tr><tr><td>Bu</td><td>ACCN</td><td>(92)^c</td></tr><tr><td>Ph</td><td>$(t\text{-Bu})_2O_2$</td><td>(94)^c</td></tr></table></td><td>205
206</td></tr>
<tr><td></td><td>MH, initiator, benzene</td><td>I<table><tr><th>R</th><th>MH</th><th>Initiator</th><th>Temp (°)</th><th>Time (min)</th><th>I</th></tr><tr><td>Me</td><td>Bu_3SnH</td><td>AIBN</td><td>80</td><td>20</td><td>(88)^c</td></tr><tr><td>Me</td><td>Ph_3SiH</td><td>Et_3B, O_2</td><td>rt</td><td>10</td><td>(88)^c</td></tr><tr><td>Me</td><td>Ph_2SiH_2</td><td>Et_3B, O_2</td><td>rt</td><td>10</td><td>(85)^c</td></tr><tr><td>OMe</td><td>Bu_3SnH</td><td>AIBN</td><td>80</td><td>20</td><td>(86)^c</td></tr><tr><td>PMP</td><td>Bu_3SnH</td><td>AIBN</td><td>80</td><td>60</td><td>(84)^c</td></tr></table></td><td>77</td></tr>
<tr><td></td><td>Bu_3SnH, toluene, reflux, 13 min</td><td>
(79)</td><td>810</td></tr>
<tr><td colspan="4">C_{13}</td></tr>
<tr><td></td><td>Bu_3SnH, AIBN, toluene, reflux</td><td>
(86)^a</td><td>811</td></tr>
<tr><td></td><td>Bu_3SnH, AIBN, toluene, 85°, 3 h</td><td>
(95)</td><td>812</td></tr>
<tr><td colspan="4">$C_{13–18}$</td></tr>
<tr><td></td><td>$Ph_2P(O)H$, $(t\text{-Bu})_2O_2$, dioxane, reflux</td><td><table><tr><th>R</th><th colspan="2">Time (h)</th></tr><tr><td>n-$C_{10}H_{21}$</td><td>6.5</td><td>(97)</td></tr><tr><td>n-$C_{14}H_{29}$</td><td>8</td><td>(87)</td></tr><tr><td>n-$C_{15}H_{31}$</td><td>6</td><td>(91)</td></tr></table></td><td>207</td></tr>
</table>

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}		Bu_3SnH, AIBN	 (99)	813
C_{15}		Bu_3SnH, toluene, reflux, 10 min	 (76)	810
	 R^1 = H, Me R^2 = Me, H	Bu_3SnH, toluene, reflux	 ("high")	814
C_{16}		Bu_3SnH, AIBN	 (92)	815
$C_{16–18}$		$Ph_2P(O)H$ (1 eq), $(t\text{-}Bu)_2O_2$ (0.45 eq), dioxane, reflux	 R — Time (h) (*E*)-$C_2H_5CH{=}CHCH_2$ — 1 — (67)[d] (*Z*)-*n*-$BuCH{=}CHCH_2$ — 1.25 — (78)[d] *n*-$BuC{\equiv}CCH_2$ — 1 — (61)[d]	207
C_{18}		Et_3SiH, dicumyl peroxide, *t*-$C_{12}H_{25}SH$ (*x* eq), solvent, reflux	 Solvent — *x* — Time (h) octane — 0 — 4 — (60) octane — 0.02 — 4 — (70–80) decane — 0.02 — 2 — (79) *m*-xylene — 0.02 — 2 — (45)	175

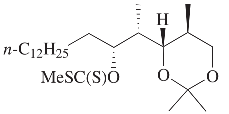
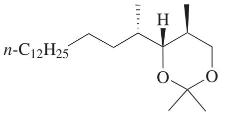
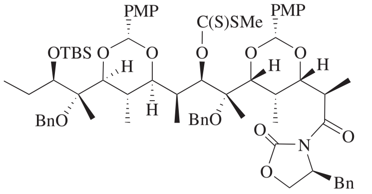
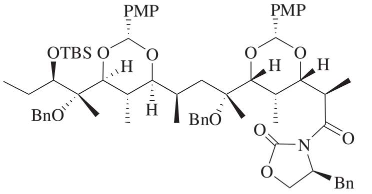
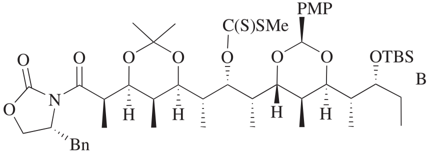
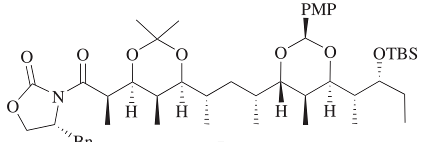
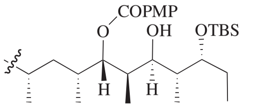
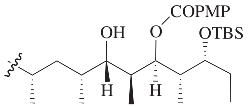
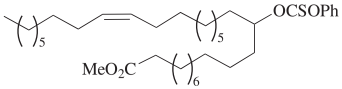
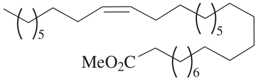
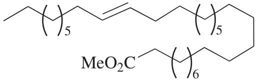
C_{20}		Bu_3SnH, AIBN, toluene, reflux	 (93)[b]	816, 817
C_{21}		Bu_3SnH, AIBN	 (55)[a]	818
C_{28}		Bu_3SnH (neat), AIBN, 110°	 **I** (84)[a]	146
		Bu_3SnH (0.03 M), AIBN, toluene, reflux	**I** (10) +  (40) +  (50)	146

TABLE 2D. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30}			
	Bu_3SnH, AIBN, toluene, 80°, 2 h	 (44)[a]	183
	$(TMS)_3SiH$, AIBN, toluene, 80°, 2 h	 (47)[a]	183

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[a] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

[b] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[c] The yield was determined by GC.

[d] The yield is based on recovered starting material.

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES

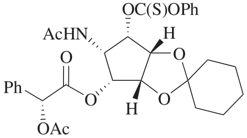
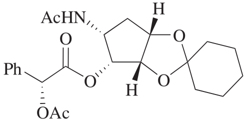
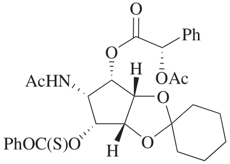
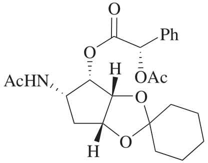
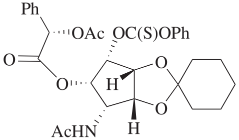
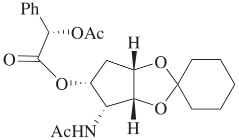
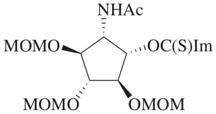
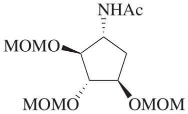
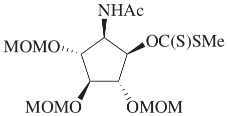
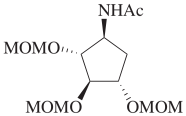
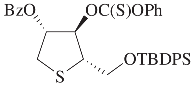
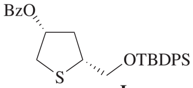
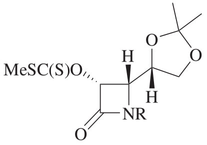
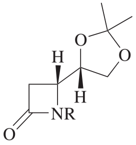
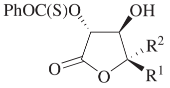
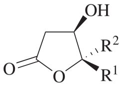
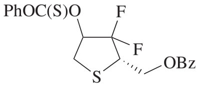
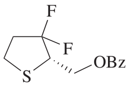
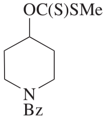
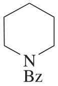
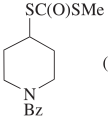
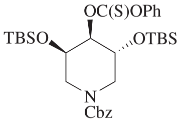
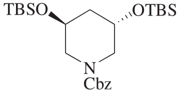
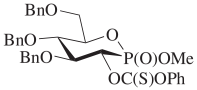
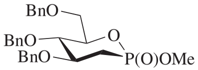
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	Bu_3SnH, AIBN	 (43)	819
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (71)	820, 821
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (77)	820, 821
	Bu_3SnH, AIBN, toluene, reflux, 30 min	 (53)	822
	Bu_3SnH, AIBN, toluene, reflux, 30 min	 (52)	822
	Bu_3SnH, toluene, reflux	 **I** (70)^a	132
	Bu_3SnH, Et_3B, benzene, 0°	**I** (70)^a	823

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 R PMP (92) Bn (90)	824
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 R^1 R^2 CH_2OTr H (84) H CH_2OTr (92)	825 826
	Bu_3SnH, AIBN, toluene, 80°, 40 min	 (80)	133
	$(n\text{-}C_{11}H_{23}CO_2)_2$, collidine, *i*-PrOH, reflux	 (53) +  (16)	32
	Bu_3SnH, AIBN, benzene	 (95)	827, 828
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (76)	829

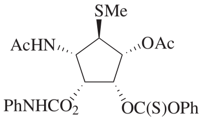
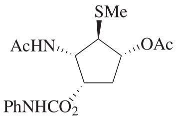
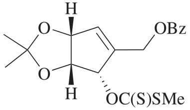
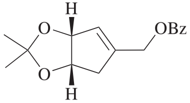
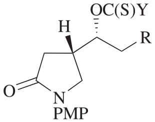
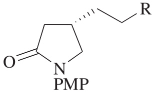
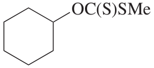
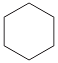
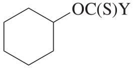
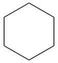
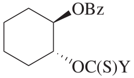
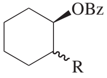
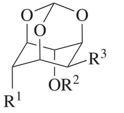
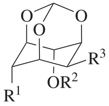
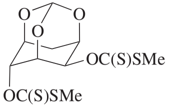
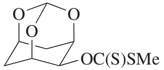
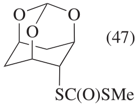
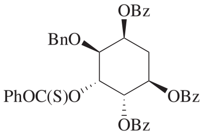
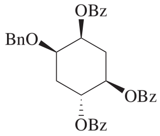
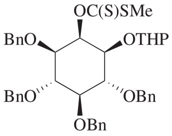
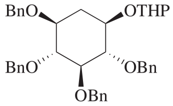
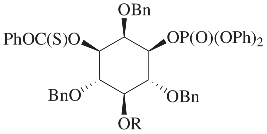
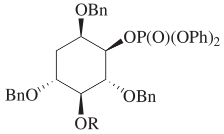
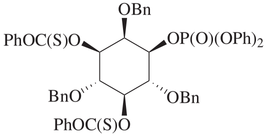
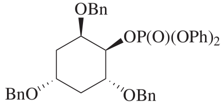
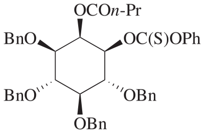
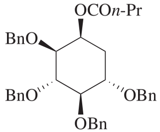
C_6		Bu_3SnH, AIBN, toluene, reflux, 1 h	 (70)	820, 821
		Bu_3SnH, AIBN, toluene, reflux, 2 h	 (88)	830, 831
$C_{6–8}$		Bu_3SnH, AIBN, solvent, reflux	 R Y Solvent OBz Im toluene (82) Et OPh benzene (98)	832
C_6		$(TMS)_2Si(Me)H$, AIBN, toluene, 80°	 $(96)^b$	184
		MH, solvent, reflux	 MH Y Solvent Temp (°) Time (h) $(MeS)_3SiH$ SMe toluene 80 — $(97)^b$ $(i\text{-}PrS)_3SiH$ SMe toluene 80 — $(98)^b$ $(TMS)_3SiH$ SMe toluene 75 2 $(86)^b$ $(TMS)_3CH$ SMe benzene 75 12 $(89)^b$ $(TMS)_3SiH$ Im toluene 75 2 $(95)^b$	185 185 178 210 178
		Bu_3SnR, solvent, reflux	 Y R Solvent Time (h) Ph H toluene 2.5 (51) NHAc H benzene 0.5 $(96)^b$ NHAc D benzene 0.5 $(88)^b$	1 77 77
	 R^1 R^2 R^3 ImC(S)O Bz OBz HO Bn OC(S)SMe	Bu_3SnH, AIBN, toluene, reflux	 R^1 R^2 R^3 H Bz OBz (56) HO Bn H (90)	30 833

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Bu_3SnH (1.0 eq), AIBN (cat.), toluene, reflux, 1.75 h	 (32) +  (47)	30
	Bu_3SnH, AIBN, toluene, reflux, 0.25 h	 (60)	834
	Bu_3SnH, AIBN, toluene, reflux, 14 h	 (72)^c	835
	Bu_3SnH, AIBN, toluene, reflux	 R H (64) TBS (70)^c	836, 837
	Bu_3SnH, AIBN, toluene, reflux	 (61)	836, 837
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (35)	838

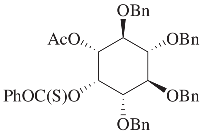
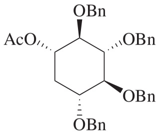
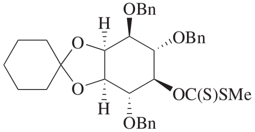
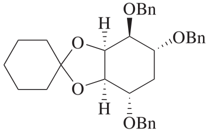
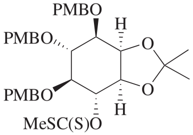
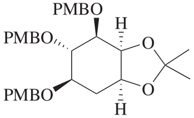
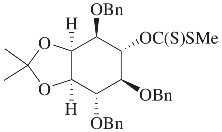
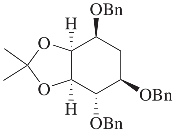
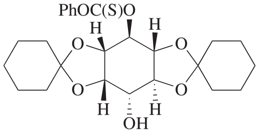
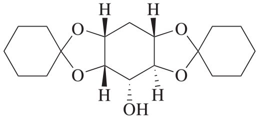
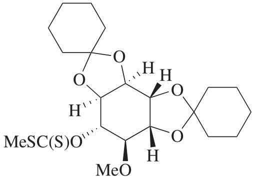
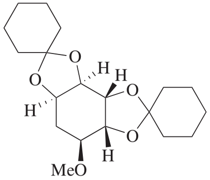
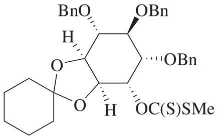
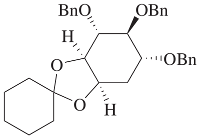
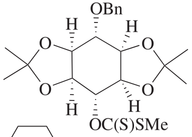
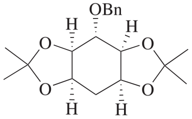
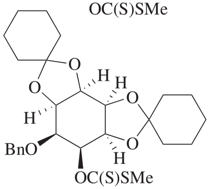
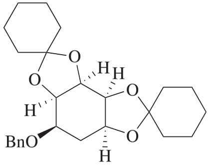
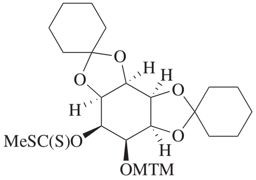
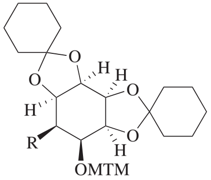
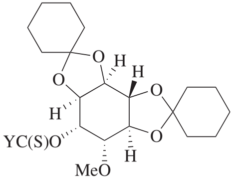
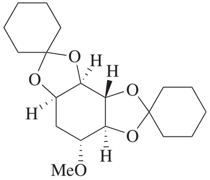
	Bu_3SnH, AIBN, toluene, reflux	 (29)[a]	839
	Bu_3SnH, AIBN, toluene, reflux, 13 h	 (80)	492
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (83)[a]	840
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (82)[a]	841
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (95)	842
	Bu_3SnH, toluene, reflux, 24 h	 (83)	843

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Bu_3SnH, toluene, reflux, 48 h	 (80)	843
	Bu_3SnH, toluene, reflux, 48 h	 (80)	843
	Bu_3SnH, toluene, reflux, 48 h	 (62)	843
	Bu_3SnH, toluene, reflux, 48 h	 **I** R = H **II** R = OH **I** + **II** (—), **I**:**II** = 1:1	843
	**A**: (n-$C_{11}H_{23}CO_2)_2$, collidine, *i*-PrOH, reflux **B**: Bu_3SnH, AIBN, toluene, reflux, 3 h	 Y **A** MeS (90) **B** Im (74)	 32 277

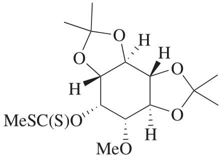
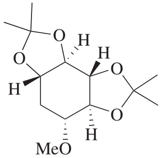
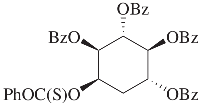
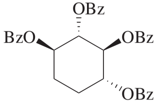
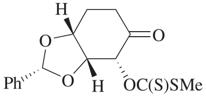
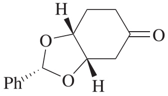
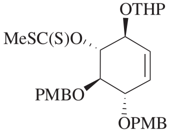
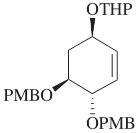
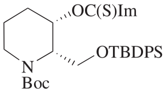
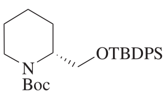
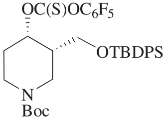
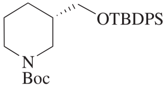
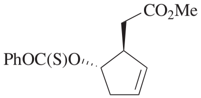
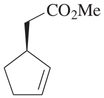
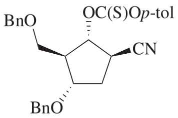
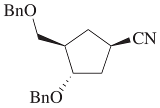
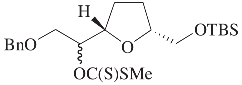
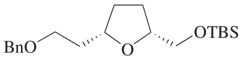
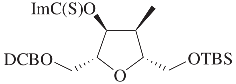
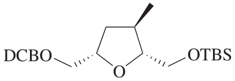
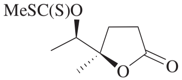
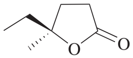
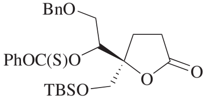
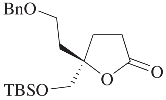
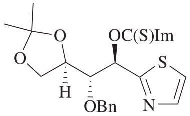
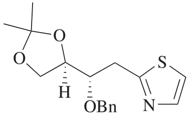
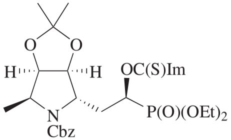
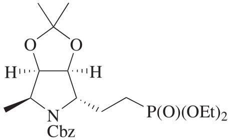
	Bu$_3$SnH, AIBN, toluene, reflux, 1 h		(89)	844
	Bu$_3$SnH, AIBN, toluene, reflux, 1 h		(99)	844
	Bu$_3$SnH, AIBN, toluene, reflux		(93)	445
	Bu$_3$SnH, AIBN, toluene, reflux, 15 h		(71)[a]	845
	Bu$_3$SnH, AIBN, toluene, reflux		(50)[a]	846, 847
	Bu$_3$SnH, AIBN, toluene, reflux		(—)	846
C$_7$				
	Bu$_3$SnH, AIBN, toluene, 75°, 4 h		(55)[c]	848

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_7$			
	Bu_3SnH, AIBN, DME, 80°, 18 h	 (53)	849
	Bu_3SnH, toluene, reflux	 (80)	850
	Bu_3SnH, AIBN, toluene, 100°	 (96)	851
	Bu_3SnH, AIBN, toluene, reflux	 (92)	852
	Bu_3SnH, AIBN, toluene, 90°, 1 h	 (95)	853
	Bu_3SnH, toluene, reflux, 6 h	 (67)[a]	854
	Bu_3SnH, AIBN, toluene, 110°, 3 h	 (76)	855

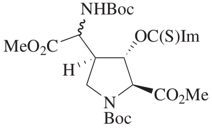
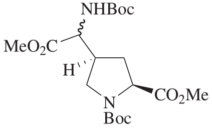
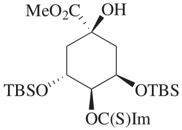
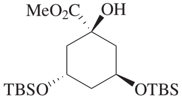
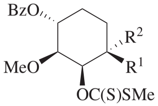
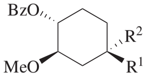
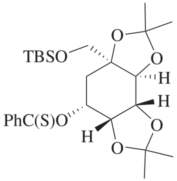
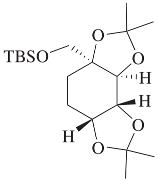
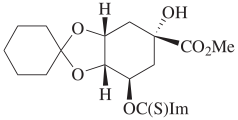
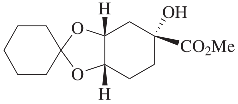
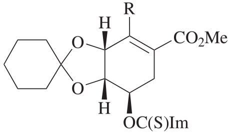
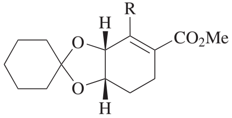
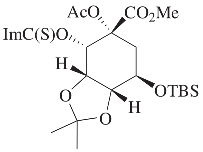
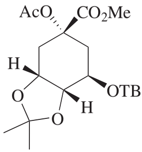
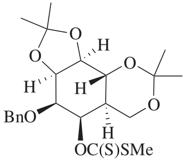
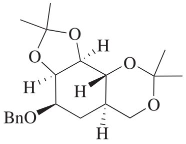
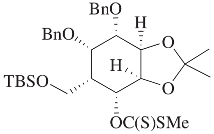
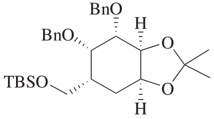
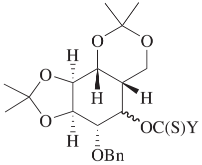
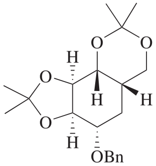
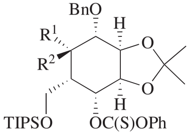
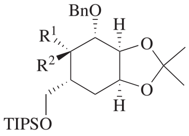
	Ph_3SnH, AIBN, benzene, reflux		(85)	856
	Bu_3SnH, AIBN, toluene, 80°, 2 h		(90)	857
	Bu_3SnH, AIBN, toluene, reflux, 2 h		R^1 / R^2 CH_2OTBS / H (92) H / CH_2OTBS (77)	858
	Bu_3SnH, AIBN, toluene, reflux, 4 h		(82)	859
	Bu_3SnH, AIBN, toluene, reflux, 3 h		(83)	231, 860
	Bu_3SnH, AIBN, toluene, reflux, 3 h		R H (72) D (80)	231, 860

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Bu_3SnH, toluene, reflux, 9 h	 (80)	861
	Bu_3SnH, AIBN, toluene, 90°	 (85)[a]	862
	Bu_3SnH, AIBN, toluene, reflux	 (70)[a]	863
	Bu_3SnH, AIBN, toluene	 Y — Temp (°) — Time (h) SMe — reflux — — — (70)[a] OPh — 85 — 0.5 — (70)	863 864
$C_{7–8}$ 	Bu_3SnH, AIBN, toluene, 85°, 0.5 h	 R^1 — R^2 BzO — H — (70)[c] $CH_2=$ — (72)	864

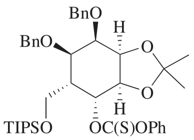
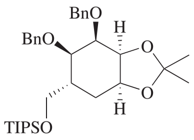
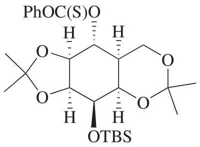
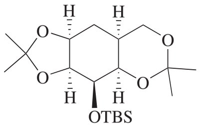
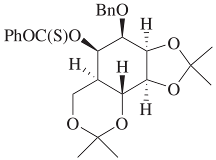
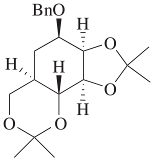
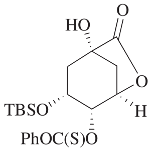
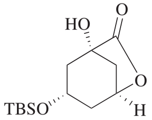
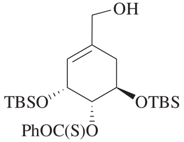
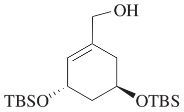
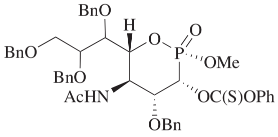
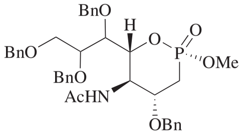
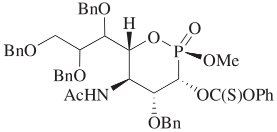
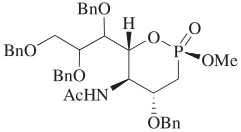
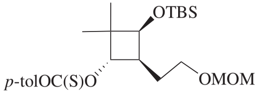
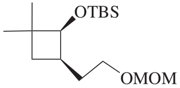
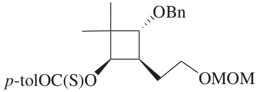
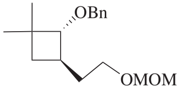
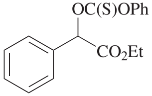
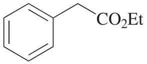
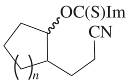
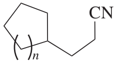
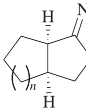
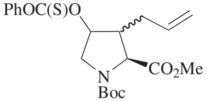
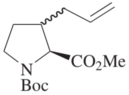
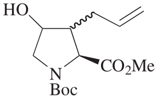
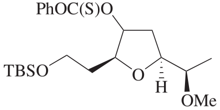
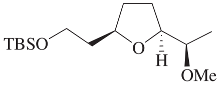
	Bu$_3$SnH, AIBN, toluene, reflux		(59)[a]	865
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h		(90)	866, 865
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h		(90)	866
	Bu$_3$SnH, AIBN, toluene, reflux, 2 h		(88)	867
	Bu$_3$SnH, AIBN, toluene, reflux, 2 h		(62)	867
	Bu$_3$SnH, AIBN, toluene, reflux, 2 h		(65)[a]	868

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Bu_3SnH, AIBN, toluene, reflux, 2 h	 $(65)^a$	868
C_8 	Bu_3SnH, AIBN, benzene, reflux	 (66)	869
	Bu_3SnH, AIBN, benzene, reflux	 $(85)^c$	869, 870
	Bu_3SnH, Et_3B, benzene, rt, 20 min	 (78)	91
C_{8-9} 	Ph_3SnH, AIBN, benzene, reflux, 20 h	 **I** +  **II** *n* **I** **II** 1 (15) (19) 2 (11) (67)	147
C_8 	Bu_3SnH, AIBN, toluene, 75–80°	 $(40)^c$ +  $(17)^c$	871
	Bu_3SnH, AIBN, benzene, reflux	 (—)	872

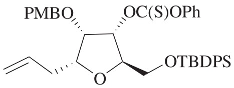
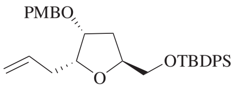
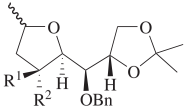
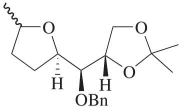
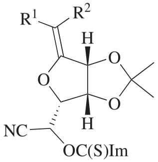
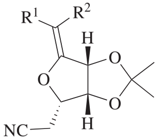
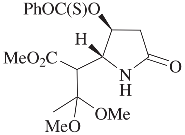
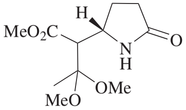
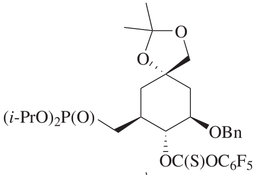
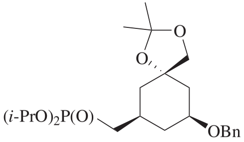
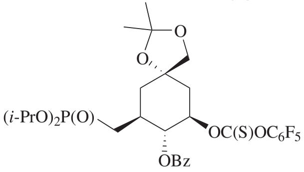
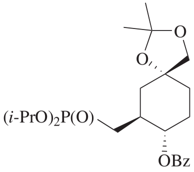
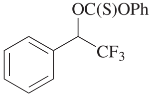
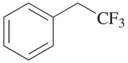
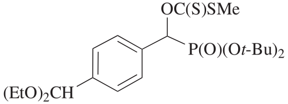
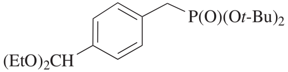
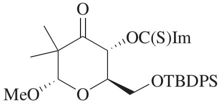
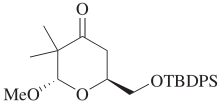
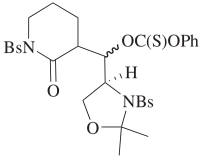
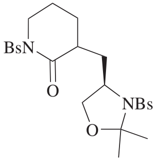
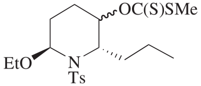
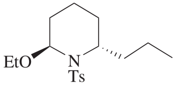
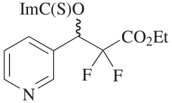
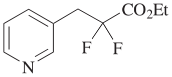
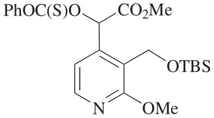
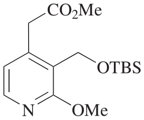
	Bu_3SnH, AIBN, benzene, reflux		(60)[c]	873
	Bu_3SnH, AIBN, toluene, reflux, 1 h		R^1 / R^2 OC(S)SMe / H (82) H / OC(S)SMe (78)	874
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 30 min		R^1 / R^2 H / CO_2Me (70)[c] CO_2Me / H (71)[c]	27
	Bu_3SnH, AIBN, benzene, reflux 0.5 h		(97)	875
	Bu_3SnH, AIBN, benzene, reflux		(96)	876
	Bu_3SnH, AIBN, benzene, reflux		(82)	876

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_8$ 	Bu_3SnH, AIBN, toluene, 80°, 3 h	 (—)	877
	Bu_3SnH, AIBN, toluene, 100°, 1 h	 (90)[c]	878
	Bu_3SnH, AIBN, toluene, 90°, 50 min	 (95)	879
	Bu_3SnH, AIBN, benzene, reflux, 0.5 h	 (80)[a]	880
	Bu_3SnH, toluene, reflux, 5 h	 (38)	881
	Bu_3SnH, toluene–CH_2Cl_2, reflux, 2 h	 (56)	882
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (99)	883

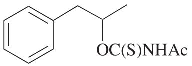
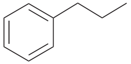
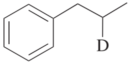
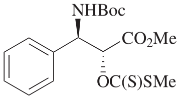
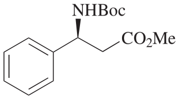
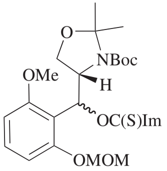
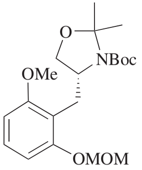
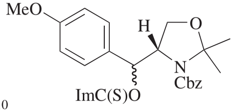
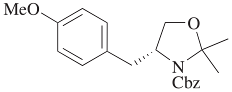
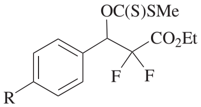
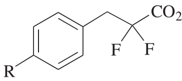
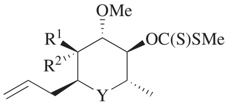
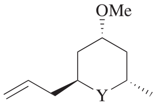
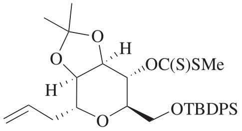
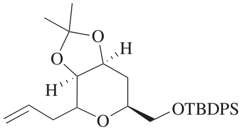
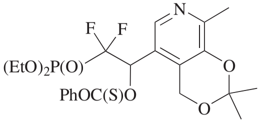
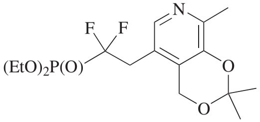
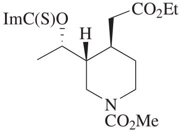
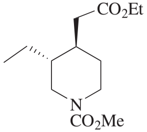
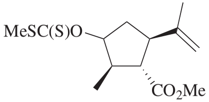
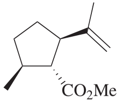
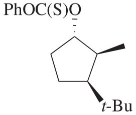
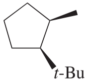
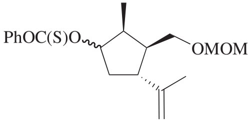
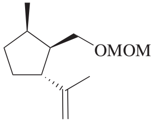
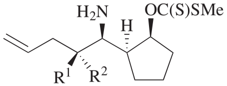
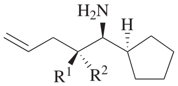
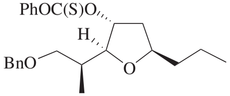
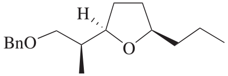
C_9		Bu_3SnH, AIBN, benzene, 80°, 20 min	 (84)[b]	77
		Bu_3SnD, AIBN, benzene, 80°, 0.5 h	 (17)	77
		Bu_3SnH, AIBN, toluene, reflux	 (80)	884
		Bu_3SnH, AIBN, toluene, reflux, 18 h	 (60)	884a
		Bu_3SnH, AIBN, toluene, reflux	 (83)[a]	885
C_{9-10}		$Ph_2P(O)H$, $(t\text{-}Bu)_2O_2$, dioxane, reflux	 R Time (h) MeO 21 (75) F 25 (72) Me 22 (83) NC 32 (62)	207
C_9		Bu_3SnH, AIBN, toluene, reflux, 1 h	 R^1 R^2 Y MeSC(S)O H O (51)[a] H MeSC(S)O ^{15}O (60)	886 887
		Bu_3SnH, AIBN, benzene, 80°, 5 min	 (92)	888

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (89)	472
	Bu_3SnH, AIBN, benzene, reflux, 3 h	 (89)	889
C_{10}			
	Bu_3SnH, AIBN, toluene, reflux	 (67)	890
	Bu_3SnH, AIBN, hexanes, reflux, 16 h	 (—)	891
	Bu_3SnH, AIBN, benzene, reflux, 0.5 h	 (88)^c	892
	Bu_3SnH, AIBN, benzene, reflux, 12 h	 R^1 R^2 H MOMO (64) MOMO H (30)	893
	Bu_3SnH, AIBN	 (53)	894

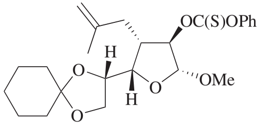
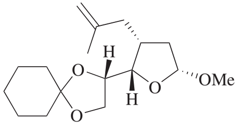
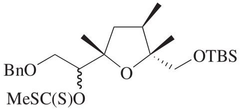
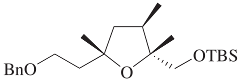
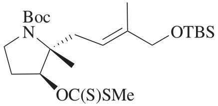
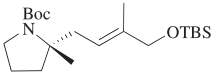
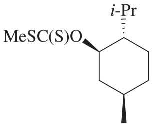
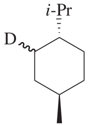
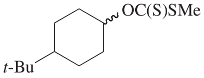
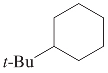
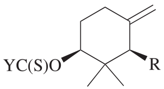
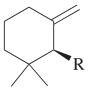
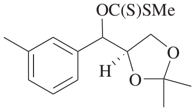
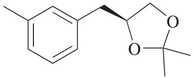
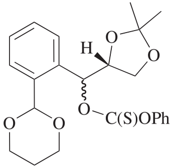
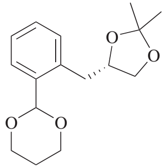
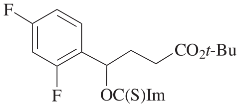
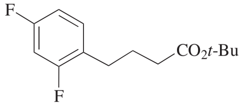
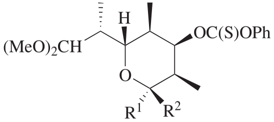
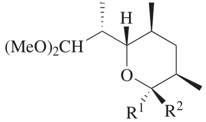
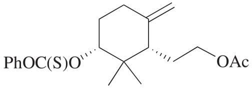
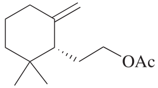
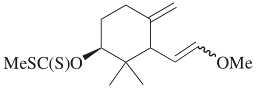
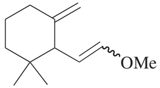
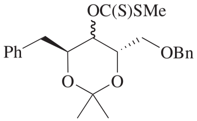
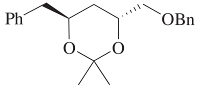
	Bu$_3$SnH, AIBN, toluene, reflux, 4 h	 (84)	895
	Bu$_3$SnH, toluene, reflux	 (80)[a]	850
	Bu$_3$SnH, AIBN, toluene	 (54)	896
	R$_3$B (*x* eq), D$_2$O (20 eq), O$_2$ (0.8 eq as air, added slowly), benzene, rt	 R *x* Me 2.5–4.0 (72)[b] *n*-Bu 5 (52)[b]	38
	(n-$C_6F_{13}CH_2CH_2)_3SnH$, AIBN, $C_6H_5CF_3$, reflux	 (55)	167
	Bu$_3$SnH, AIBN, toluene, reflux	 Y R PhO CO$_2$Me (30)[c] Im CO$_2$Me (30)[c] PhO CH$_2$OTBS (40)[c] Im CH$_2$OPiv (75)[c]	897
	Bu$_3$SnH, toluene, reflux	 (66)	898

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Bu_3SnH, AIBN, toluene, 100°, 0.75 h	 (69)[a]	899
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 (96)	900
	Bu_3SnH, AIBN, toluene, 90°, 6 h	 R^1 R^2 OMe H (85) H OMe (60)	901
C_{11}			
	Bu_3SnH, AIBN, toluene, 100°, 3 h	 (66)[c]	902
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (90)[a]	903
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (91)	155, 904

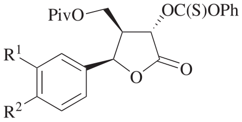
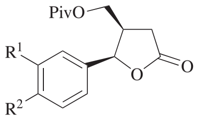
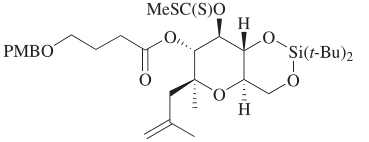
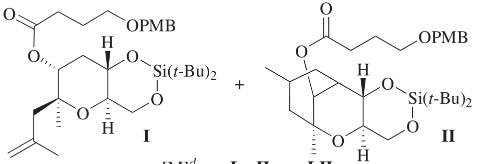
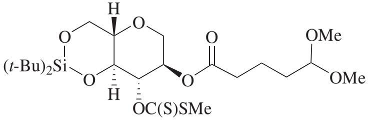
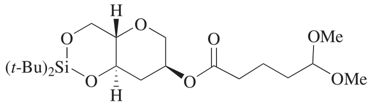
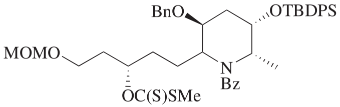
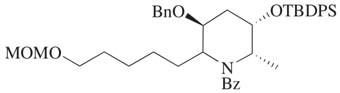
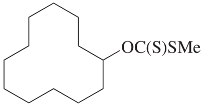
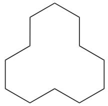
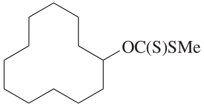
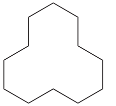
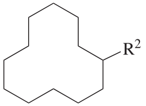
	Bu_3SnH, AIBN, toluene, reflux, 0.5–1 h	 R^1 / R^2 MeO / MeO (100) —OCH_2O— (87)	905 906
	Bu_3SnH, AIBN, benzene, reflux	 I + II [M][d] / I + II / I:II 0.135 / (90) / >95:5 0.014 / (60) / 1:1.4 0.003 / (50) / <5:95	58
	Bu_3SnH, AIBN, toluene, reflux	 (72)[a]	907
	Bu_3SnH, AIBN, benzene, reflux	 (95)	908
C_{12}			
	$PhSiH_3$, AIBN, toluene, reflux, 1 h	 **I** (100)[b]	367, 72
	Bu_3SnH, Et_3B, benzene, rt, 20 min	**I** (93)	91
	Ph_3SiH, Et_3B, O_2, toluene, rt	**I** (73)[c]	367

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	$Ph_2SiHSiHPh_2$, AIBN, EtOAc, reflux, 16 h	 **I** (81)	186
	$(TMS)_3SiH$, ACCN, H_2O, reflux, 4 h	**I** (98)	909
	EPHP (10 eq), initiator (*x* eq), CTAB (*y* eq), solvent	**I** Initiator | Solvent | *x* | *y* | Temp | Time (h) | **I** Et_3B | MeOH | 10 | 0 | rt | 2.4 | (89) Et_3B | $MeOH–H_2O^e$ | 10 | 0 | rt | 10 | (48) Et_3B | H_2O | 10 | 2 | rt | 10 | (42) ACVA | H_2O | 0.75 | 2 | 80° | 8 | (73)	199
	H_3PO_2, AIBN, $NaHCO_3$, EtOH, reflux, 0.5 h	**I** (100)	202
	$R_4N^+ H_2PO_2^-$ (3 eq), ACVA (*x* eq), H_2O, reflux	**I** R_4N | *x* | **I** *n*-$C_{16}H_{33}NMe_3$ | 0.5 | (94) (*n*-Bu)$_4$N | 0.75 | (90) (*n*-Bu)$_3$NMe | 0.75 | (62) Me_4N | 0.75 | (45)	201
	$R_2P(O)H$, initiator, dioxane, reflux, 16–35 h	**I** R | **I** *n*-Bu | (89–94)^b Ph | (67–92)^b initiator = AIBN, ACCN, Bz_2O_2, (*t*-Bu)$_2O_2$, *t*-BuOOBz, or *t*-BuOOCO$_2$*i*-Pr)	205, 206
	 $_3$GeH, initiator, solvent, 1 h	**I** Initiator | Solvent | Temp | **I** Et_3B | THF | rt | (80) V-70 | H_2O | 80° | (63)	188 910
	$HGaCl_2$ (2 eq), Et_3B (0.2 eq), THF, rt, 6 h	**I** (84)	191
	$(R^1)_3B$ (5 eq), $(R^2)_2O$ (*x* eq), O_2 (0.8 eq as air, added slowly), benzene, rt	 R^1 | R^2 | *x* | Me | H | 5 | (99)^b Me | D | 20 | (67)^b Et | D | 20 | (63)^b *n*-Bu | D | 20 | (83)^b	38

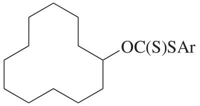
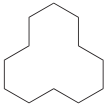
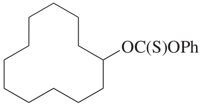
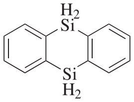
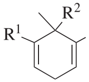
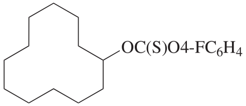
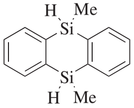
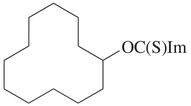
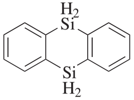
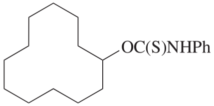
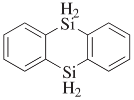
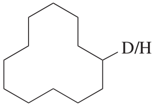
	MH, Et_3B, O_2, benzene, rt, 10 min	 **I** Ar | MH | Ph | Ph_2SiH_2 | (91) $4\text{-}FC_6H_4$ | Ph_2SiH_2 | (96) $4\text{-}FC_6H_4$ | $(TMS)_3SiH$ | (98)	173
	Polystyrene-linked Bu_2SnH, AIBN, $(MeO)_3SiH$, BuOH, toluene, reflux, 36 h	**I** (65)	156
	Bu_3SnH, Et_3B, benzene, rt, 20 min	**I** (88)	91
	Bu_3SnH, AIBN, toluene, 80–100°	**I** (68)	92
	PMHS (5 eq), $(Bu_3Sn)_2O$ (cat.), BuOH (5.5 eq), AIBN, toluene, 80–100°	**I** (66)	92
	$(TMS)_3SiH$, ACCN, H_2O, reflux, 4 h	**I** (89)	909
	 , AIBN, toluene, 80°, 2 h	**I** (96)^b	187
	 , AIBN, hexanes, reflux, 15 h	**I** R^1 | R^2 | **I** H | TIPS | (91) OMe | TBS | (74)	209
	 , AIBN, benzene, reflux, 4 h	**I** (87)	76

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	 , AIBN, toluene, 80°, 2 h	**I** (46)^b	187
	$(TMS)_3SiH$, ACCN, H_2O, reflux, 4 h	**I** (90)	909
	MH, initiator, solvent	**I**	

MH	Initiator	Solvent	Temp	Time (h)	**I**	Refs.
Et_3SiH	AIBN	benzene	140°^{f}	5	(75)^b	39
Ph_3SiH	$(t\text{-}Bu)_2O_2$	octane	reflux	3	(90)^b	39
Ph_3SiH	Et_3B	benzene	rt	0.2	(93)^b	39
$(TMS)_3SiH$	AIBN	benzene	reflux	3	(95)^b	39
$(TMS)_3SiH$	Et_3B	benzene	rt	0.2	(89)^b	39
Bu_3SiH	AIBN	benzene	reflux	3	(88)^b	39
$(TMS)_3SiH$	ACCN	H_2O	reflux	4	(84)	909

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	 , AIBN, toluene, 80°, 2 h	**I** (32)^b	187
	MD, initiator (x eq), solvent		39

MD	Initiator	x	Solvent	Temp (°)	Time (h)		% D-Content
Ph_3SiD	$(t\text{-}Bu)_2O_2$	0.2	chlorobenzene	130	5	(92)^b	18
$(TMS)_3SiD$	AIBN	0.2	benzene	80	2	(83)^b	80
$(TMS)_3SiD$	Et_3B	1.2	benzene	rt	1	(85)^b	41
Bu_3SnD	AIBN	0.2	benzene	80	3	(98)^b	98

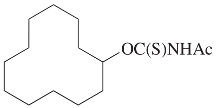
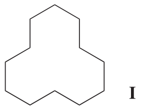
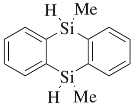
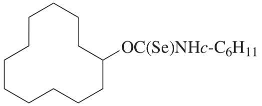
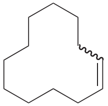
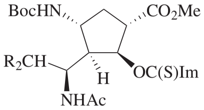
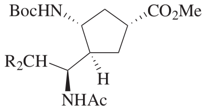
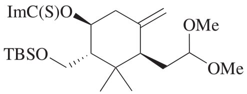
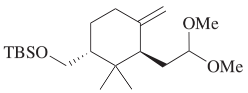
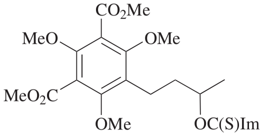
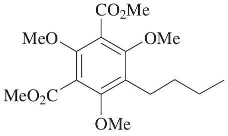
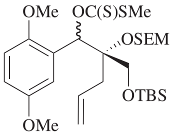
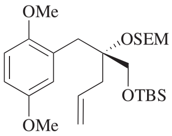
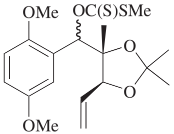
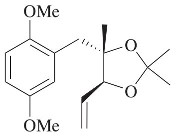
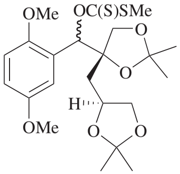
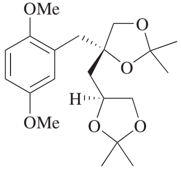
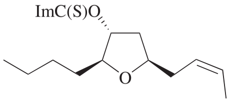
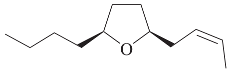
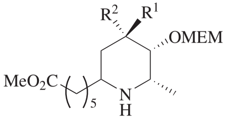
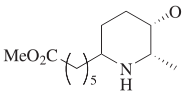
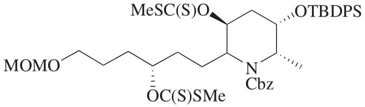
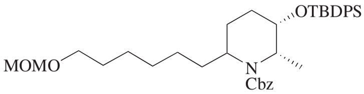
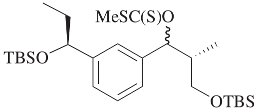
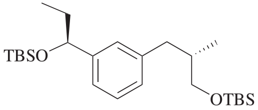
	Bu_3SnH, AIBN, benzene, 80°, 20 min	 **I** (88)^b	77
	Ph_3SiH, Et_3B, O_2, benzene, rt, 10 min	**I** (91)^b	77
	 , AIBN, benzene, reflux, 4 h	**I** (100)^b	76
	Bu_3SnH, Et_3B, O_2, benzene, rt	**I** (67) +  (33)	78
C_{12-14} 	Bu_3SnH, AIBN, toluene, 100°, 15 min	 R Et (95) *n*-Pr (91)	911 912
C_{12} 	Bu_3SnH, Et_3B, O_2, toluene	 (81)	913
	$(TMS)_3SiH$, AIBN, toluene, sealed tube, 125°	 (85)	914
	Bu_3SnH, AIBN, toluene, reflux	 (82)^a	915

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Bu_3SnH, AIBN, toluene, 2.5 h	 (60)	916
	Bu_3SnH, AIBN, toluene, reflux, 12 h	 (86)[a]	917, 813
	Bu_3SnH, AIBN	 (—)	918
	Bu_3SnH, toluene, reflux	 R^1 / R^2 OC(S)Im / H (93)[a] H / OC(S)Im (81)[a]	919
	Bu_3SnH, AIBN, benzene, reflux	 (99)	920
C_{13}			
	Bu_3SnH, AIBN, toluene	 (94)	921

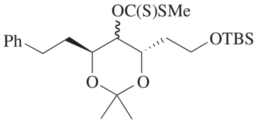
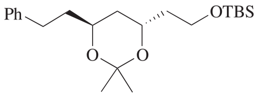
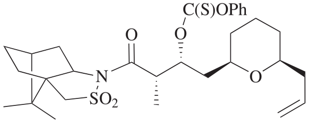
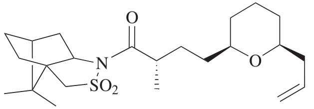
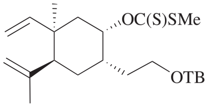
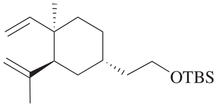
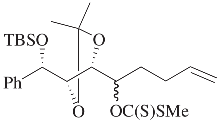
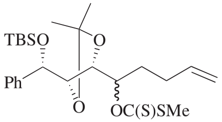
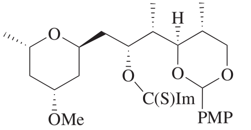
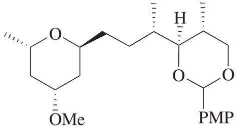
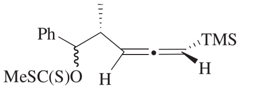
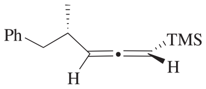
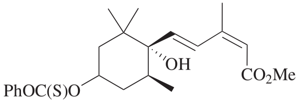
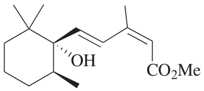
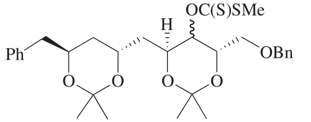
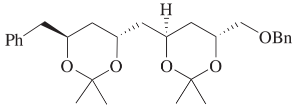
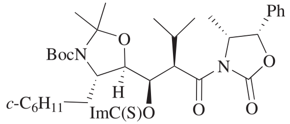
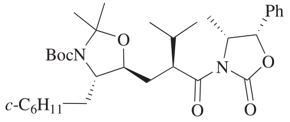
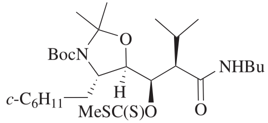
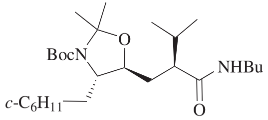
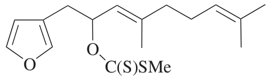
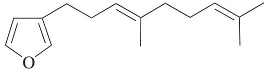
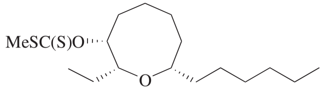
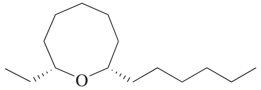
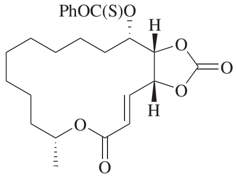
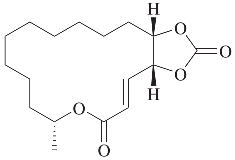
	Bu$_3$SnH, AIBN, toluene, reflux		(93)[a]	922
	Bu$_3$SnH, AIBN, benzene, reflux, 7 h		(87)	923
C$_{14}$				
	Bu$_3$SnH, AIBN, toluene, 90°, 1 h		(100)	924
	Bu$_3$SnH, AIBN, benzene, reflux, 2 h		(94)	925
	Bu$_3$SnH, toluene, reflux, 0.5 h		(95)	926
C$_{15}$				
	Bu$_3$SnH, AIBN, toluene, 90°		(71)	927
	Bu$_3$SnH, AIBN, toluene, 70°, 2 h		(15)[c]	928

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{15}				
	Bu_3SnH, AIBN, toluene, 100°		$(72)^c$	904
	Bu_3SnH, toluene, reflux		(91)	929
	Bu_3SnH, toluene, reflux		(88)	929
	Bu_3SnH		("low")	930
	Bu_3SnH, AIBN, benzene, reflux		(75)	931
C_{16}				
	Bu_3SnH, AIBN, toluene, 80–85°, 7.5 h		(53)	932

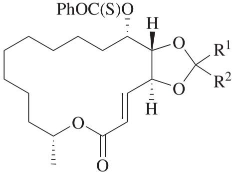
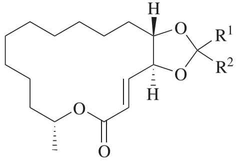
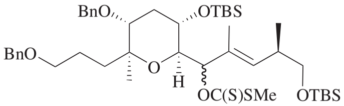
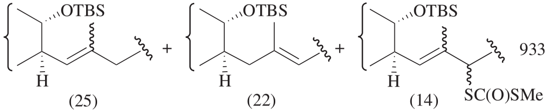
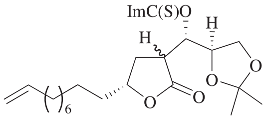
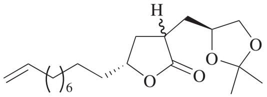
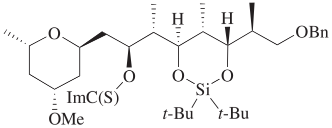
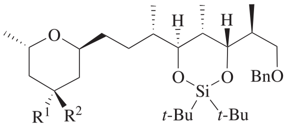
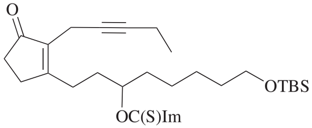
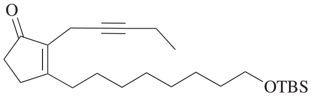
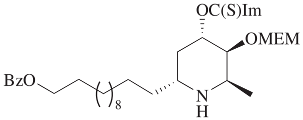
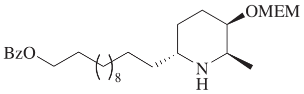
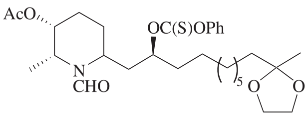
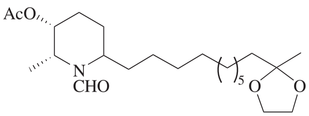
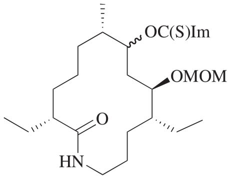
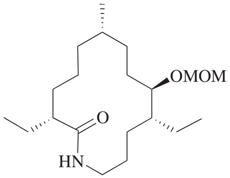
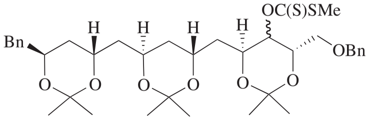
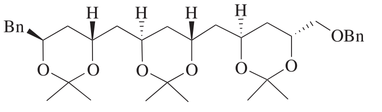
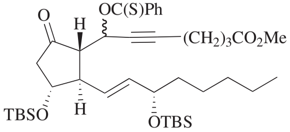
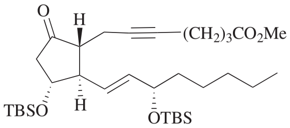
C_{16}			
	Bu_3SnH, AIBN, toluene, 80–85°	 R^1 R^2 Time (h) Me Me 2.5 (49) O= 4 (89)	932
	Bu_3SnH, AIBN, benzene, reflux	 (25) + (22) + (14)	933
C_{17}			
	Bu_3SnH, toluene, gentle warming	 (70)	934
	Bu_3SnH (*x* eq), AIBN, toluene, reflux	 *x* **I** **II** 10 (96) (0) 1.5 (—) (trace) **I** R^1 = OMe, R^2 = H **II** R^1 = H, R^2 = OMe	935, 936
C_{18}			
	Bu_3SnH, AIBN, toluene, reflux	 (33)	937
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (74)	938

TABLE 2E. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	Bu_3SnH, $(t\text{-}BuOOCO)_2$ (added in portions), acetone, rt, 30 h	 (83)	939
	Bu_3SnH, toluene, reflux, 3 h	 (95)	940
C_{19} 	Bu_3SnH, AIBN, toluene, 100°	 (62)[c]	904
C_{20} 	Bu_3SnH, $(t\text{-}Bu)_2O_2$, toluene, reflux	 (98)	941, 229

[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] The yield was determined by GC.

[c] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

[d] This value is the initial molarity of the starting material.

[e] The solvent was 1:1 v/v $MeOH–H_2O$.

[f] A sealed tube was used.

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES

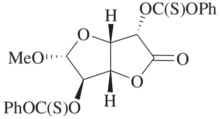
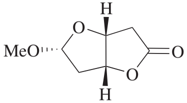
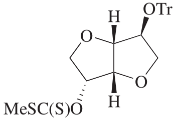
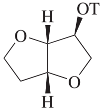
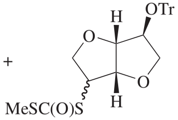
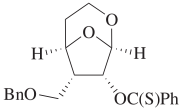
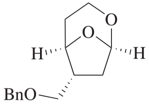
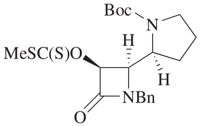
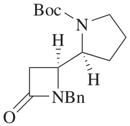
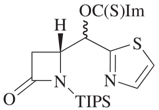
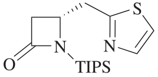
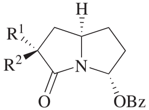
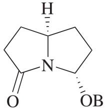
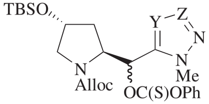
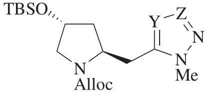
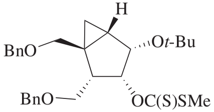
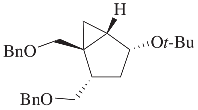
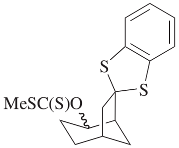
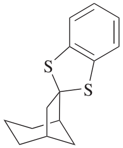
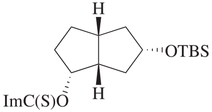
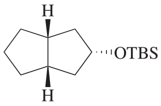
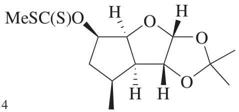
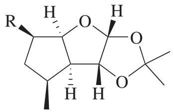
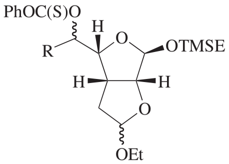
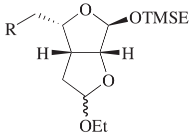
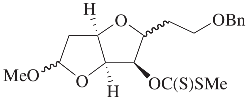
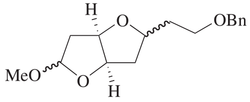
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	Bu_3SnH, toluene, 80°, 3 h	 (83)	942, 943
	$(n\text{-}C_{11}H_{23}CO_2)_2$, *i*-PrOH, collidine, reflux	 (77)[a] +  (4)	32
C_7			
	Bu_3SnH, AIBN, toluene, 75°, 1 h	 (66)	529
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (80)	944
	Ph_3SnH, AIBN, benzene, reflux, 0.75 h	 (83)	159
	Bu_3SnH, AIBN, benzene, 80°, 3 h	 R^1 — R^2 H — PhOC(S)O (65) PhOC(S)O — H (58)	945
	Bu_3SnH, AIBN, toluene, reflux, 7 h	 Y — Z N — CH (85)[b] CH — N (100)[b]	946

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		Bu_3SnH, Et_3B, benzene, rt	 (79–90)[b]	717, 716
		Bu_3SnH	 (—)	947
		Bu_3SnH, AIBN, toluene, reflux, 40 min	 (80)	948
		Bu_3SnH, AIBN, toluene, reflux, o/n	 R H (9) HO (33) MeO (15)	949
$C_{8–14}$		Bu_3SnH, AIBN, benzene, reflux, 4 h	 R Me (76) n-C_7H_{15} (97)	950
C_8		Bu_3SnH, AIBN, toluene, reflux, 6 h	 (69)	951

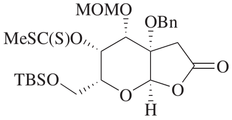
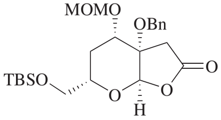
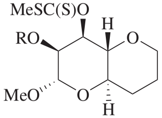
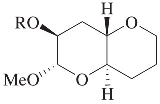
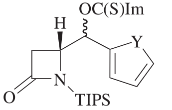
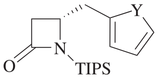
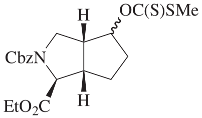
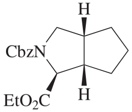
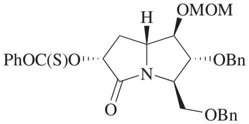
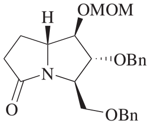
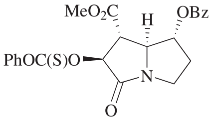
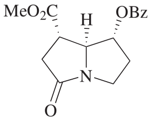
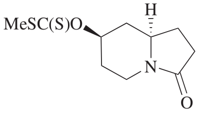
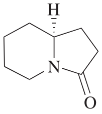
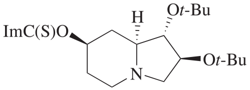
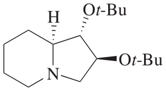
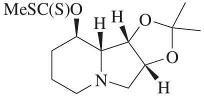
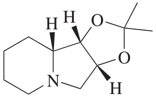
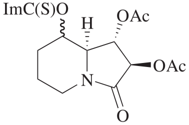
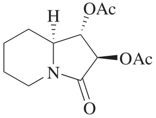
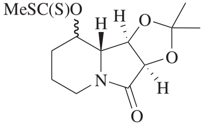
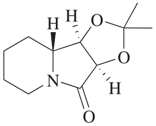
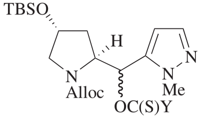
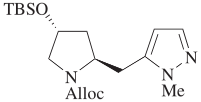
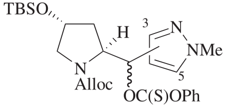
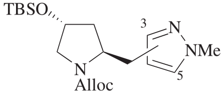
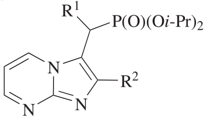
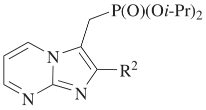
C_8		Bu_3SnH, AIBN, toluene, reflux	 (70)	952
		Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 R Bn (63) PMB (61)	475
		Ph_3SnH, AIBN, benzene, reflux, 0.75 h	 Y O (71) S (67)	159
		Bu_3SnH, AIBN, toluene	 (66)[b]	953
		Bu_3SnH, AIBN, benzene, reflux	 (58)	954
		Bu_3SnH, AIBN, benzene, reflux	 (87)	955
		Bu_3SnH, AIBN, benzene, reflux, 7 h	 (69)	218

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	Bu_3SnH, AIBN, toluene, reflux, 16 h	 (68)	956
	Bu_3SnH, xylenes, reflux, 48 h	 (62)	957
	Bu_3SnH, AIBN, toluene, reflux	 (60)	958
	Bu_3SnH, AIBN, toluene, reflux	 (68)[b]	958
	Bu_3SnH, AIBN	 Y SMe (83) OPh (98)	959
	Bu_3SnH, AIBN, toluene, reflux, 7 h	 Isomer 3- (56) 5- (73)	946
C_{8-13}			
	Bu_3SnH, AIBN, toluene, 80°	 R^1 / R^2 PMPOC(S)O Me (87) PMPOC(O)S Me (33) PMPOC(S)O Ph (88) PMPOC(O)S Ph (29)	960

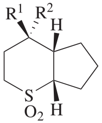
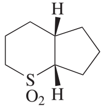
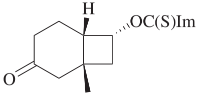
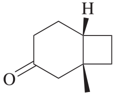
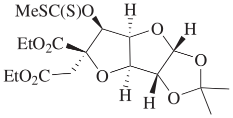
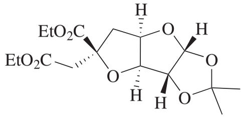
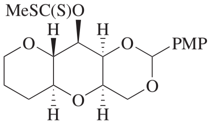
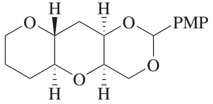
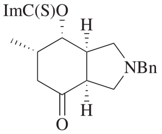
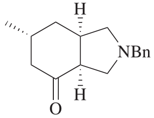
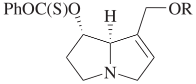
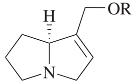
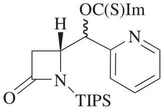
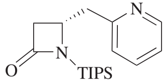
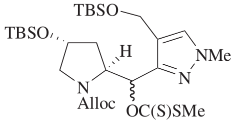
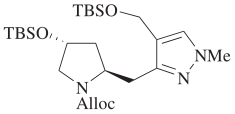
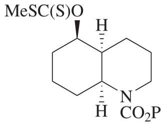
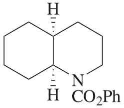
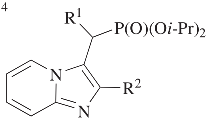
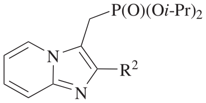
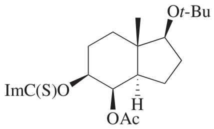
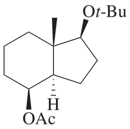
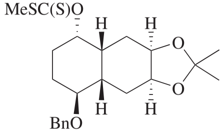
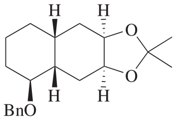
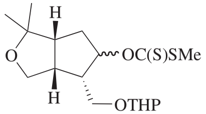
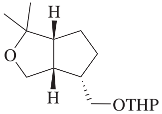
C_8	 $R^1 = OC(S)SMe; R^2 = H$ $R^1 = H; R^2 = OC(S)SMe$	Bu_3SnH, AIBN, toluene, reflux, 7 h	 (77)	961
C_9		Bu_3SnH, AIBN, benzene, 100°, 1 h	 (35)	962
		Bu_3SnH, AIBN, toluene, reflux, 4 h	 (69)	963
		Bu_3SnH, AIBN, toluene, reflux, 1 h	 (75)	475
		Bu_3SnH, AIBN, toluene, reflux, 2 h	 (93)	964
		Bu_3SnH, AIBN, toluene, 75°, 3 h	 R TBS (66) Bz (64)	965
		Ph_3SnH, AIBN, benzene, reflux, 45 min	 (83)	159

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (56)^b	946
	Bu_3SnH, AIBN, toluene	 (78)	966
C_{9-14} 	Bu_3SnH, AIBN, toluene, 80°	 R^1 | R^2 PMPOC(S)O | Me | (92) PMPOC(O)S | Me | (85) PMPOC(S)O | Ph | (92) PMPOC(O)S | Ph | (98)	960
C_{10} 	Bu_3SnH, AIBN, toluene, reflux, ia, 3 h	 (81)	967, 968
	Bu_3SnH, AIBN, toluene, 70°	 (—)	969
	Bu_3SnH, AIBN, benzene, reflux, 20 h	 (70)^b	970

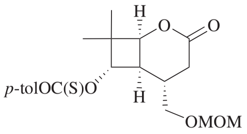
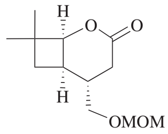
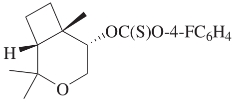
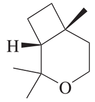
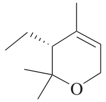
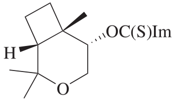
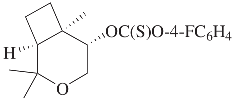
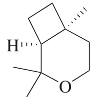
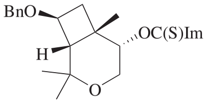
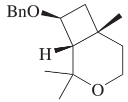
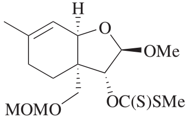
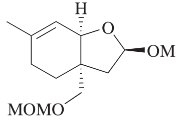
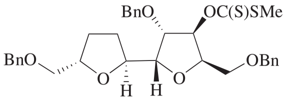
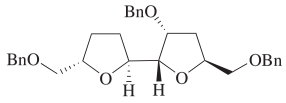
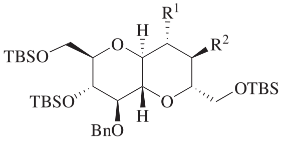
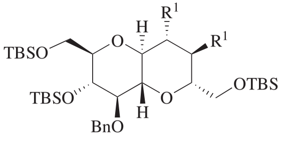
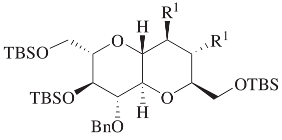
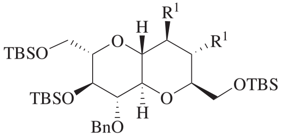
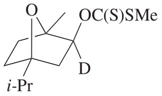
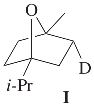
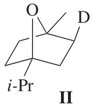
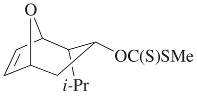
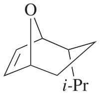
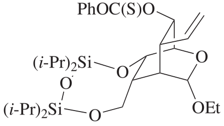
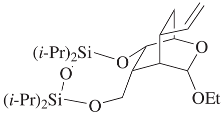
	Bu_3SnH, AIBN, benzene, reflux	 (61)	869
	Bu_3SnH, AIBN, toluene, reflux	 **I** +  **II** **I** + **II** (—), **I**:**II** = 43:57	141, 142
	Bu_3SnH, AIBN, toluene, ia, 90°	**I** (79)	141, 142
	Bu_3SnH, AIBN, toluene, reflux	**I** + **II** (—), **I**:**II** = 65:35	142
	Bu_3SnH, AIBN, toluene, ia, 100°	**I** (80)	142
	Bu_3SnH, AIBN, toluene, ia, 90°	 (75)	142
	Bu_3SnH, AIBN, toluene, 100°	 (93)	971
	Bu_3SnH, AIBN, benzene, reflux, 6 h	 (90)	972
	Bu_3SnH, AIBN, toluene, 90°, 3 h	 (94)	973

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}  R^1 = OC(S)SMe; R^2 = TBSO R^1 = TBSO; R^2 = OC(S)SMe	Bu_3SnH, AIBN, toluene, reflux, 1 h	 R^1 R^2 H TBSO $(45)^b$ TBSO H $(25)^b$	57
 R^1 = OC(S)SMe; R^2 = TBSO R^1 = TBSO; R^2 = OC(S)SMe	Bu_3SnH, AIBN, toluene, reflux, 1 h	 R^1 R^2 H TBSO $(50)^b$ TBSO H $(45)^b$	57
	Bu_3SnH	 **I** +  **II** **I** + **II** (94), **I**:**II** = 10:1	974
	Bu_3SnH, AIBN, benzene, reflux, 10 h	 (95)	975
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (60)	976

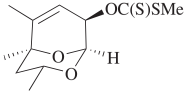
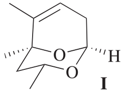
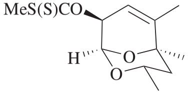
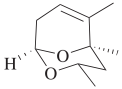
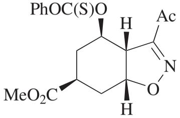
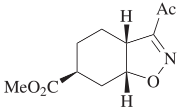
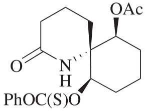
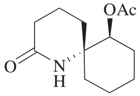
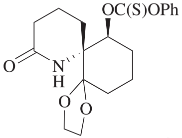
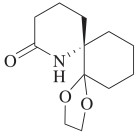
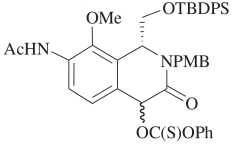
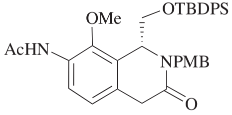
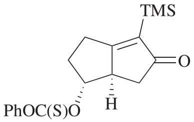
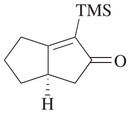
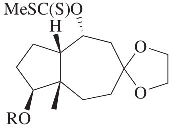
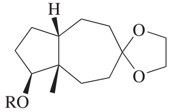
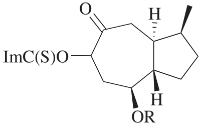
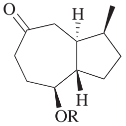
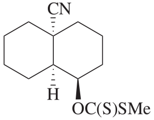
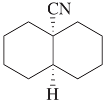
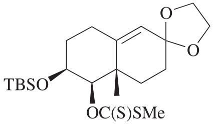
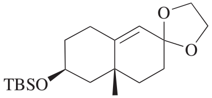
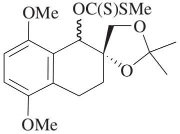
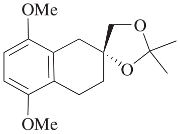
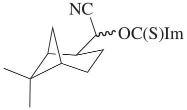
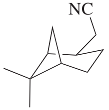
C_{10}		Bu_3SnH, toluene, reflux	 **I** (40)[c]	977
		Bu_3SnH, AIBN, toluene, 60°, 3.5 h	**I** (76)	978
		Bu_3SnH, toluene, reflux	 (53)	977
		Bu_3SnH, AIBN, benzene, reflux, 2 h	 (74)	106, 979
		Bu_3SnH, AIBN, toluene, 95°	 (93)	880
		Bu_3SnH, AIBN, toluene, 95°, 1.5 h	 (90)	880
		Bu_3SnH, AIBN, benzene, reflux	 (54)[b]	981
C_{11}		Bu_3SnH, AIBN, toluene, reflux	 (60)[b]	982

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	Bu_3SnH, toluene, reflux, 24 h	 R Ac (38)^c Bz (38)^c	983
	Bu_3SnH, toluene, reflux	 R TBS (87) THP (87)^b	984
	Bu_3SnH, AIBN	 (—)	985
	Bu_3SnH, AIBN, toluene, reflux	 (22)^c	986
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 (70)^b	987, 813
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 30 min	 (75)^c	27

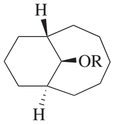
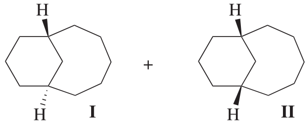
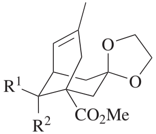
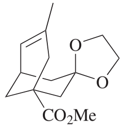
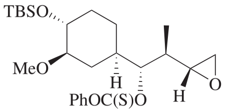
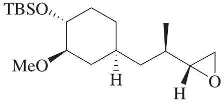
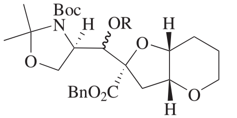
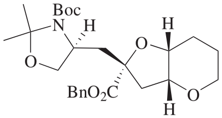
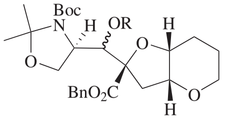
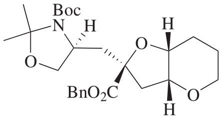
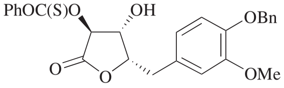
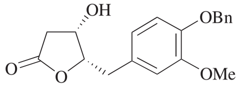
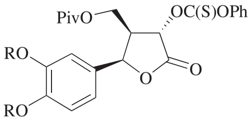
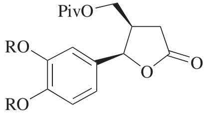
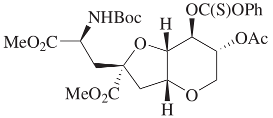
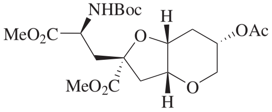
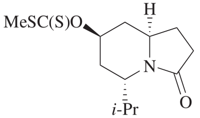
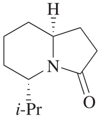
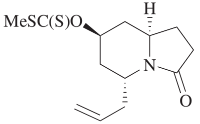
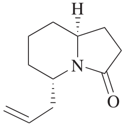
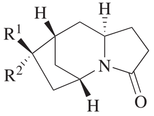
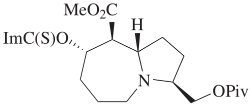
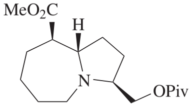
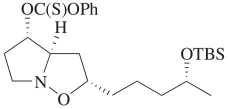
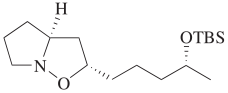
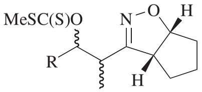
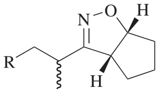
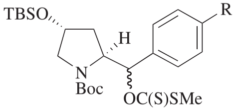
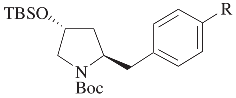
 R = C(S)SMe	Bu$_3$SnH (x eq), benzene, reflux	 x / **I + II** / **I:II** 1.1 / (53) / 1:5.4 5 / (—) / 1:1 10 / (—) / 2:1	988
	Bu$_3$SnH, AIBN, toluene, reflux, 1.5 h	 R^1 / R^2 ImC(S)O / H / (42)^b H / ImC(S)O / (60)^b	989
	Bu$_3$SnH, AIBN, benzene, reflux	 (80)	990
 R = C(S)SMe	Bu$_3$SnH, AIBN, toluene, reflux	 (81)^b	991
 R = C(S)SMe	Bu$_3$SnH, AIBN, toluene, reflux	 (66)^b	991
	Bu$_3$SnH, AIBN, toluene, reflux	 (73)^b	992
	Bu$_3$SnH, AIBN, toluene, reflux, 1 h	 R / R —CH$_2$— / (87) Me / Me / (100)	905 906

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	Bu_3SnH, AIBN, toluene, reflux	 (78)	993
	Bu_3SnH, toluene, reflux, 24 h	 (80)	994
	Bu_3SnH, toluene, reflux, 17 h	 (19) +  R^1 R^2 H Me (25) Me H (50)	994
	Bu_3SnH, AIBN, toluene, 100°, 0.5 h	 (96)	995
C_{11} 	Bu_3SnH, AIBN	 (52)[b]	996
C_{11-15}  R = Et, *i*-Pr, *t*-Bu, Ph	Bu_3SnH, AIBN, benzene, reflux, 1 h	 (—)	997
C_{11-12} 	Bu_3SnH, AIBN, toluene, reflux	 R H (68)[c] CH_2OTBS (73)[c]	998

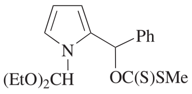
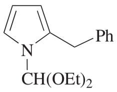
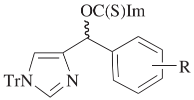
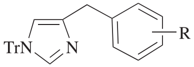
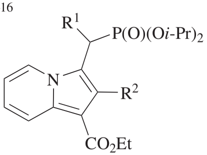
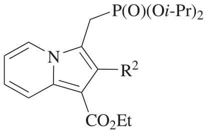
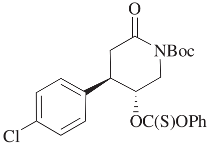
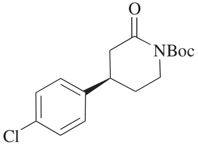
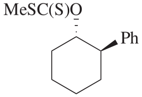
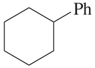
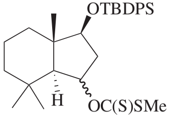
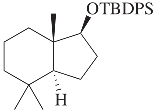
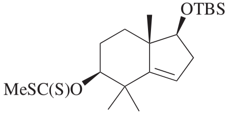
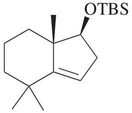
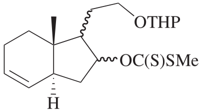
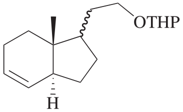
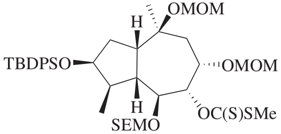
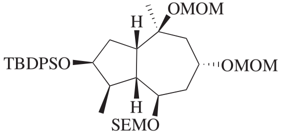
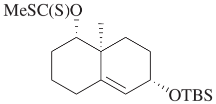
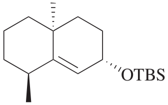
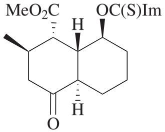
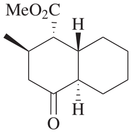
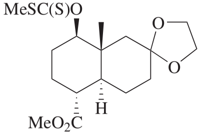
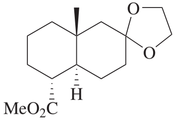
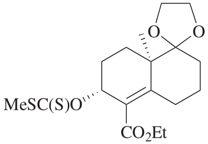
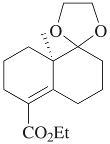
C_{11}			Bu_3SnH, AIBN, benzene, reflux, 28 h	 (83)	999
		R = 3-CN, 4-CN, 4-CH(OEt)$_2$	Bu_3SnH, AIBN, toluene, reflux	 (—)	1000
C_{11-16}			Bu_3SnH, AIBN, toluene, 80°	 R^1 / R^2 PMPOC(S)O / Me (92) PMPOC(O)S / Me (78) PMPOC(S)O / Ph (73) PMPOC(O)S / Ph (76)	960
C_{11}			Bu_3SnH, (t-BuOOCO)$_2$, acetone, rt, 18 h	 (85)^b	1001
C_{12}			(n-$C_6F_{13}CH_2CH_2$)$_3$SnH, AIBN, $C_6H_5CF_3$, reflux	 (89)	167
			Bu_3SnH, AIBN, toluene, reflux, 15 min	 (92)^b	1002
			Bu_3SnH, AIBN, toluene, sealed tube, 150°, 10 min	 (98)^b	1003, 1004

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Bu_3SnH, toluene, ia, reflux, 22 h	 (58)	1005
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (79)	1006
	Bu_3SnH, AIBN, benzene, reflux, 1.5 h	 (56)	1007
	Bu_3SnH, AIBN, benzene, 60°, 1 h	 (93)	1008
	Bu_3SnH, AIBN, toluene, reflux	 (92)	1009
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (68)	1010

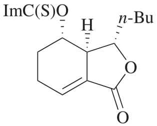
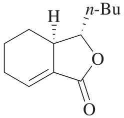
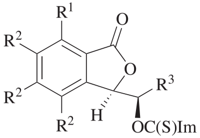
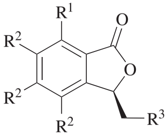
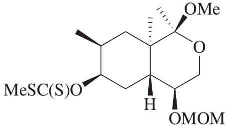
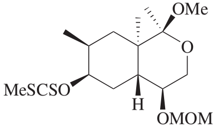
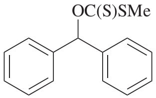
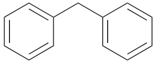
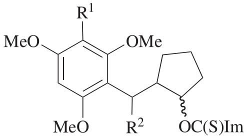
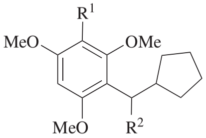
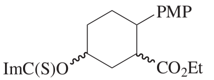
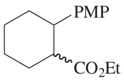
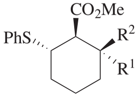
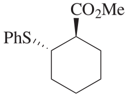
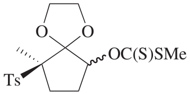
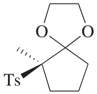
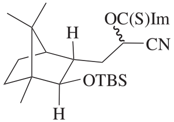
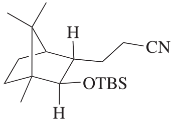
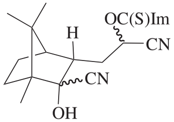
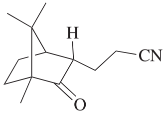
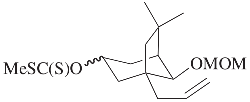
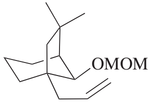
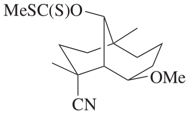
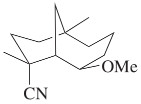
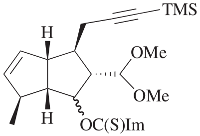
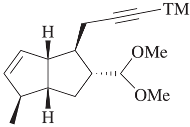
	Bu$_3$SnH, AIBN, toluene, reflux, 4 h	 (68)	1011
C$_{12–15}$ 	Bu$_3$SnH, AIBN, toluene, reflux, 0.25 h	 R^1 R^2 R^3 OBn H *n*-Pr (80) H OBn *n*-C$_6$H$_{13}$ (90)	1012, 1013
C$_{12}$ 	Bu$_3$SnH, AIBN, toluene, reflux	 (67)^b	1014
C$_{13}$ 	Bu$_2$P(O)H, (*t*-Bu)$_2$O$_2$, dioxane, reflux, 16 h	 (85)	205
C$_{13–16}$ 	(TMS)$_3$SiH, AIBN, toluene, sealed tube, 125°	 R^1 R^2 CO$_2$Me H (88) H *i*-Bu (99)	914
C$_{13}$ 	Bu$_3$SnH, AIBN, toluene, 90°	 (74)^c	1015

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 R^1 R^2 H OC(S)Im (52) OC(S)Im H (57)	1016
	Bu_3SnH	 (74)	1017
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 0.5 h	 (70)^c	27
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 0.5 h	 (82)^c	27
	Bu_3SnH, AIBN	 (90)	1018, 1019
	Bu_3SnH, toluene, reflux	 (43)^c	1020
	Bu_3SnH, AIBN, toluene, reflux, 0.75 h	 (57)^b	1021

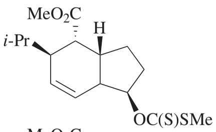
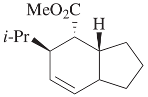
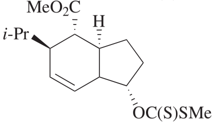
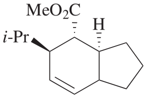
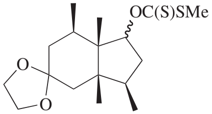
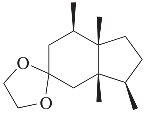
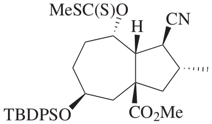
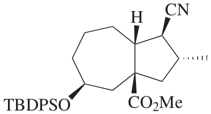
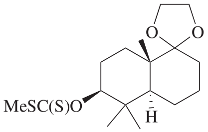
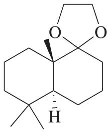
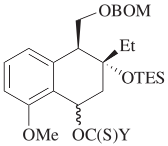
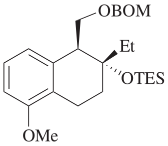
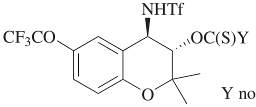
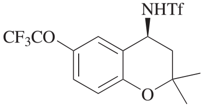
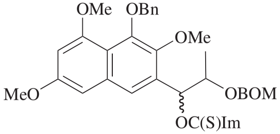
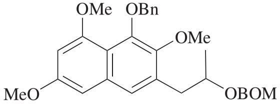
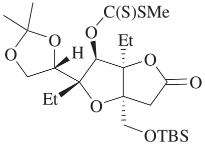
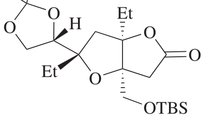
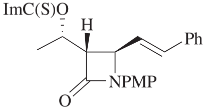
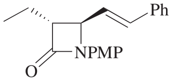
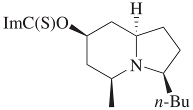
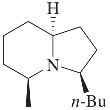
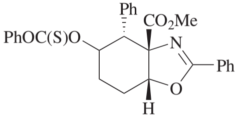
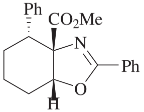
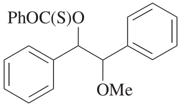
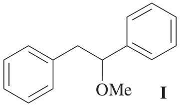
	Bu_3SnH, toluene, reflux, 7.5 h	 (49)	1022
	Bu_3SnH, toluene, reflux, 7.5 h	 (55)	1022
	Bu_3SnH, toluene, reflux	 (84)[b]	1023
	Bu_3SnH, AIBN, toluene	 (82)[c]	1024
	Bu_3SnH, AIBN, xylene, reflux, 0.5 h	 (92)	1025
	Bu_3SnH, AIBN	 Y: Im (61) SMe (0)	1026
 Y not specified	Bu_3SnH	 (—)	1027

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		Bu_3SnH, toluene, reflux	 (82)^c	618
		Bu_3SnH, AIBN, toluene, reflux	 (73)^c	1028
		Bu_3SnH, AIBN, toluene, 70°, 4 h	 (<10)	1029
		Bu_3SnH, toluene, reflux, 16 h	 (70)	1030
		Bu_3SnH, AIBN, toluene, 100°, 5 h	 (91)	1031
C_{14}		PMHS (5 eq), $(Bu_3Sn)_2O$ (cat.), BuOH (5.5 eq), AIBN, toluene, 80–100°	 **I** (70)	92
		Bu_3SnH, AIBN, toluene, 80–100°	**I** (65)	92

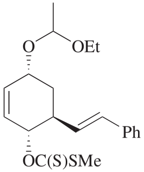
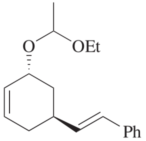
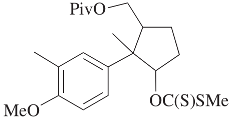
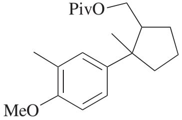
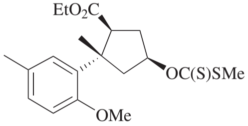
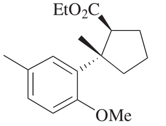
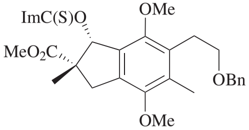
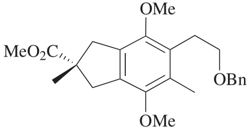
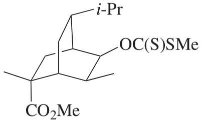
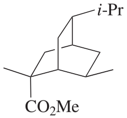
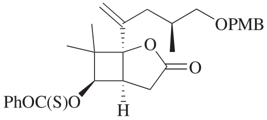
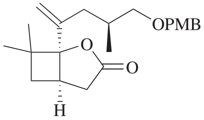
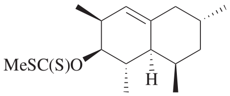
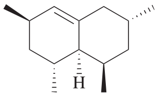
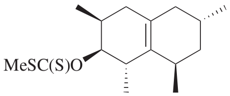
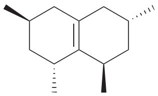
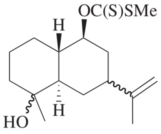
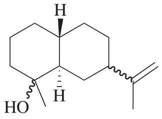
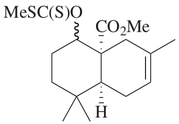
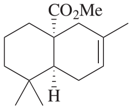
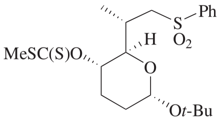
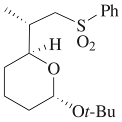
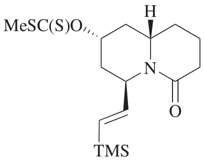
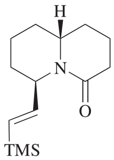
	Bu_3SnH, AIBN, toluene		(82)	1032
	Bu_3SnH, AIBN, toluene, reflux, 3 h		(83)	1033
	Bu_3SnH, AIBN, toluene, reflux, 40 min		(98)[b]	1034, 1035
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h		(75)	1036, 1037
	Bu_3SnH, AIBN, toluene, reflux, 4 h		(81)	1038
	Bu_3SnH, AIBN, benzene, reflux, 5 h		(99)	1039

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	$(TMS)_3SiH$, AIBN	 (73)^b	1040
	$(TMS)_3SiH$, AIBN	 (—)	1040
	Bu_3SnH, AIBN, toluene, reflux	 ("low")	1041
	Bu_3SnH, AIBN, benzene, reflux, 10 h	 (71)	1042, 1043
	Bu_3SnH, AIBN, toluene, 90°, 7 h	 (—)	1044
	Bu_3SnH, toluene, reflux, 14 h	 (81)	1045

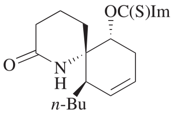
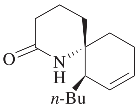
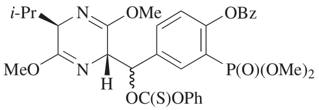
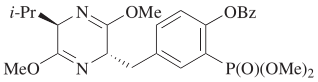
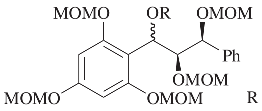
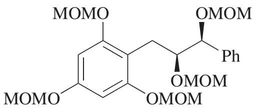
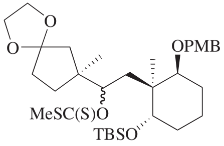
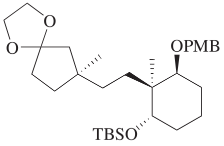
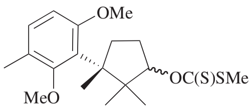
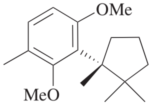
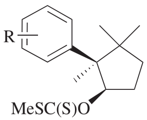
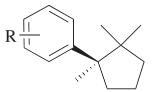
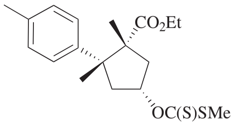
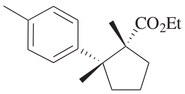
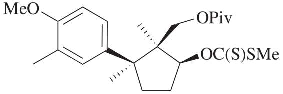
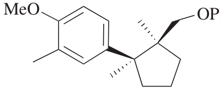
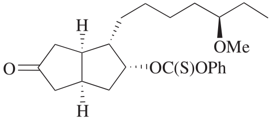
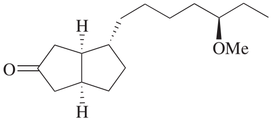
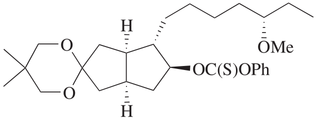
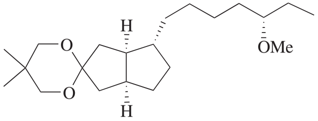
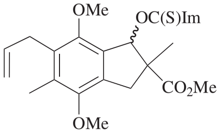
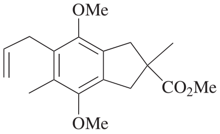
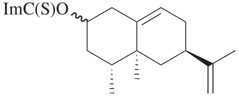
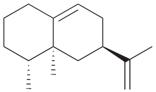
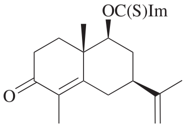
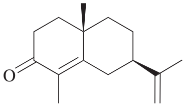
		Bu$_3$SnH, AIBN, toluene, reflux, 2 h	 (65)	1046
		Bu$_3$SnH, AIBN, toluene, 70°	 (71)^c	1047
C$_{15}$				
	 R = C(S)SMe	Bu$_3$SnH, AIBN, benzene, reflux, 2 h	 (91)	1048
		Bu$_3$SnH, AIBN, toluene, reflux, 2 h	 (89)	1049
		Bu$_3$SnH, AIBN, benzene, reflux, 3 h	 (75)	1050
		Bu$_3$SnH, AIBN, toluene, reflux, 4 h	 R 3-Me (35)^b 4-Me (30)^b	1051
		Bu$_3$SnH, AIBN, toluene, reflux, 40 min	 (96)	1052

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (80)	1053
	Bu_3SnH, AIBN, toluene, 90°, 2.5 h	 (89)	1054
	Bu_3SnH, AIBN, toluene, 90°, 2.5 h	 (77)	1054
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 (83)	1055
	Bu_3SnH, benzene	 (65)	1056
	Bu_3SnH, toluene, reflux, 2 h	 (82)	1057

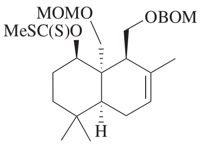
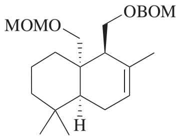
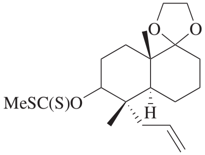
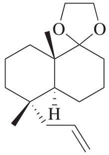
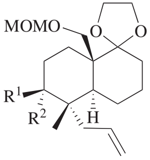
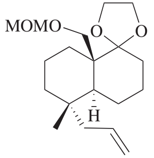
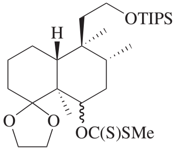
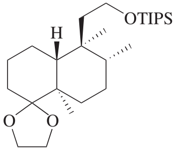
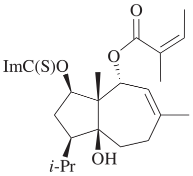
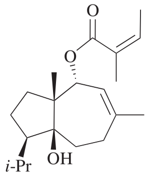
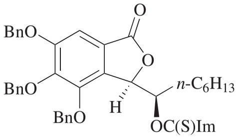
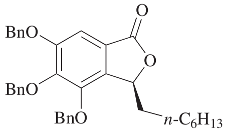
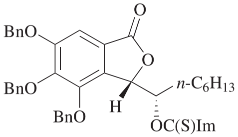
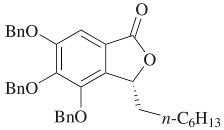
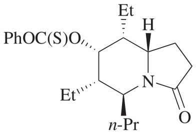
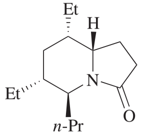
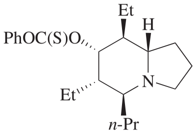
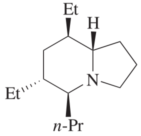
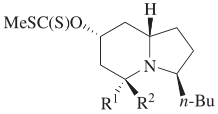
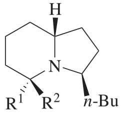
	Bu_3SnH, AIBN, toluene, reflux	 (93)[c]	1058
	Bu_3SnH, AIBN, xylene, reflux	 (86)	1059
	Bu_3SnH, AIBN, xylene, 150°, 6 min	 R^1 — R^2 MeSC(S)O — H (82) H — MeSC(S)O (64)	1060 1061
	Bu_3SnH, xylene, 150°, 0.25 h	 (89)	1062, 1063
	Bu_3SnH, AIBN, benzene, reflux, 4 h	 (14)	1064

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	Bu_3SnH, AIBN, toluene, reflux, 0.25 h	 (90)	1013
	Bu_3SnH, AIBN, toluene, reflux, 0.25 h	 (84)	1013
	Bu_3SnH, AIBN, toluene, 100°, 3 h	 (88)	1065
	Bu_3SnH, AIBN, toluene, 100°, 3 h	 (74)	1066
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 R^1 R^2 *n*-Pr H (79) H *n*-Pr (38)	1067

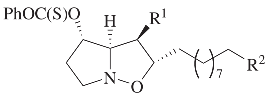
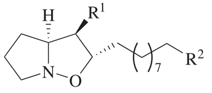
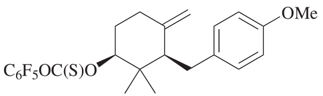
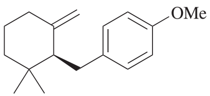
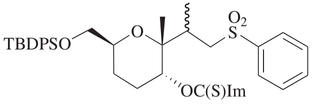
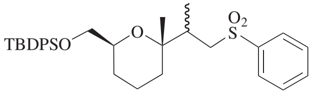
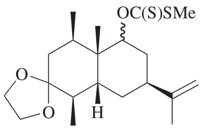
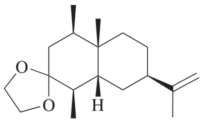
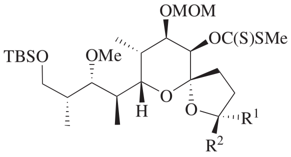
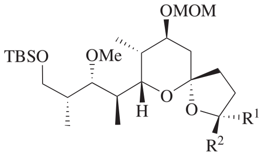
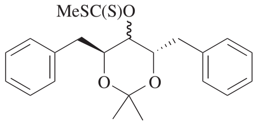
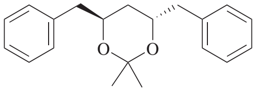
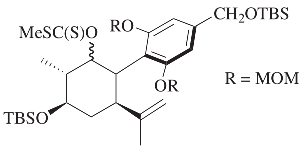
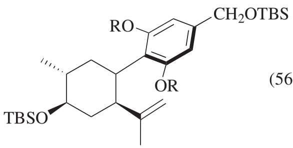
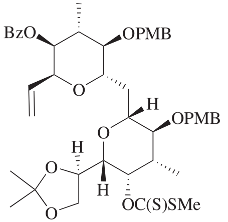
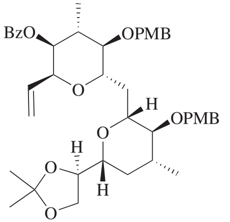
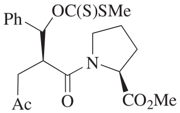
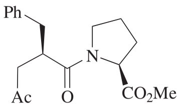
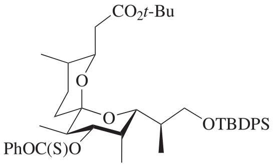
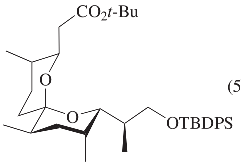
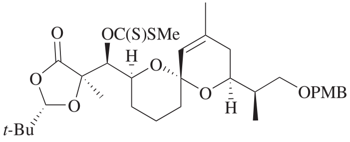
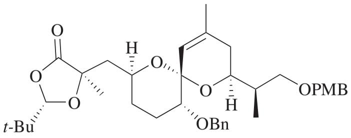
C_{15-16}				
	Bu_3SnH, AIBN		R^1 R^2 H H (94) CH_2OTBS OPMP $(51)^b$	1068
C_{16}				
	Bu_3SnH, AIBN, benzene, reflux		(77)	1069
	Bu_3SnH, AIBN, toluene		(—)	1070
	Bu_3SnH, AIBN, toluene, reflux		(86)	1071
	$PhSiH_3$, Bz_2O_2, toluene		R^1 R^2 CH_2OBz H $(76)^c$ H CH_2OBz $(58)^c$	1072
C_{17}				
	Polystyrene-linked Bu_2SnH, AIBN, benzene, reflux, 20 h		(75)	155

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
 R = MOM	Bu_3SnH, AIBN, toluene, 90°	 (56)[c]	1073
	Ph_3SnH, AIBN, benzene, reflux	 (90)	1074
	Bu_3SnH, AIBN, toluene, 80°, 8 h	 (68)	391
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (58)[b]	1075
	Bu_3SnH, AIBN, toluene, 80°	 (88)[b]	1076, 1077, 1078

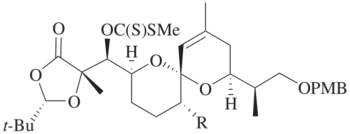
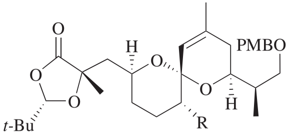
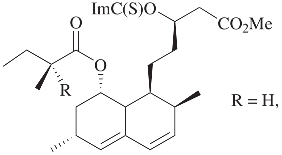
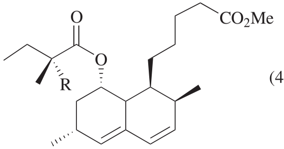
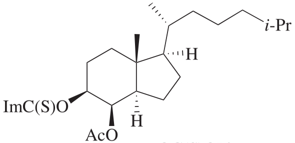
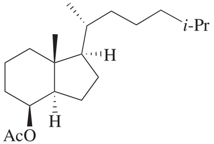
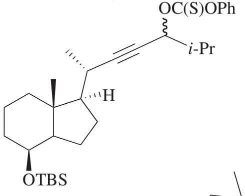
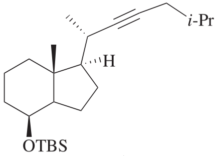
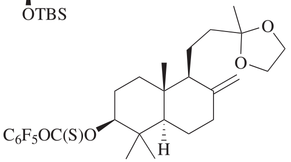
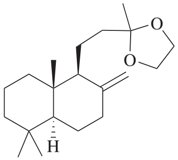
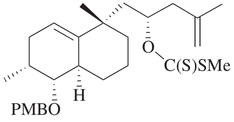
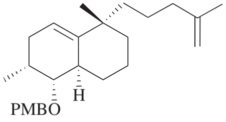
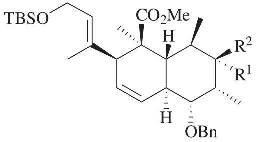
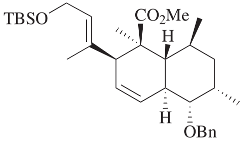
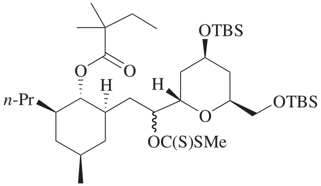
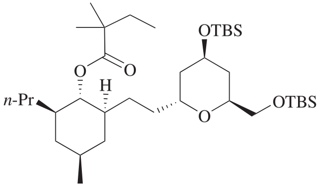
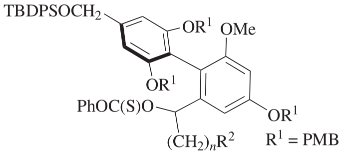
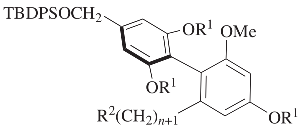
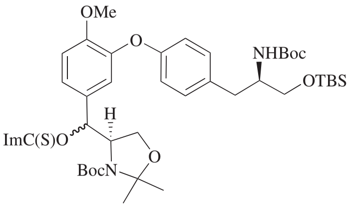
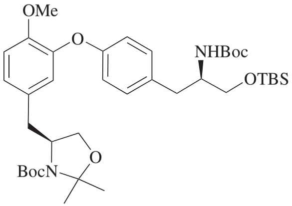
		Bu$_3$SnH, AIBN, toluene, 80°		R OBn (86)^b H (70)^b	1077 1078
	 R = H, Me	Bu$_3$SnH, AIBN, toluene		(45–55)	1079
C$_{18}$		Bu$_3$SnH, AIBN, toluene, reflux		(75)	1080
		Bu$_3$SnH, AIBN, toluene, reflux, 3 h		(98)^b	1081
		Bu$_3$SnH, AIBN, benzene, reflux, 4 h		(80)	1082
		Bu$_3$SnH, AIBN, toluene, reflux, 0.25 h		(82)	407

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	Bu_3SnH, AIBN, toluene, reflux	 R^1 / R^2 OC(S)Im / H (82)[b] H / OC(S)Im (35)[c]	1083
	Bu_3SnH, AIBN, toluene	 (98)	1084
C_{18-21} 	Bu_3SnH, AIBN, toluene, 75°, 12 h	 R^2 / n CH_2=CH / 3 (97) CH_2=CH / 5 (82) MeC≡C / 3 (83) MeC≡C / 5 (76)	1085
C_{18} 	Bu_3SnH, AIBN, toluene	 (96)	1086

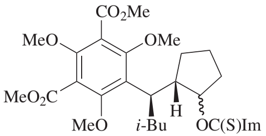
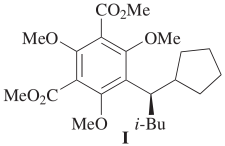
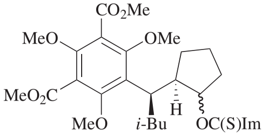
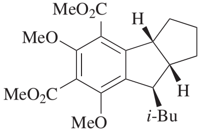
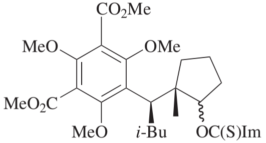
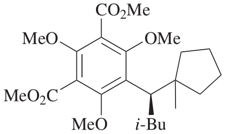
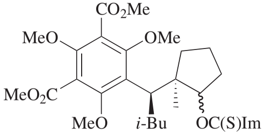
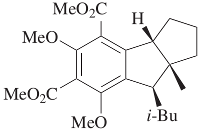
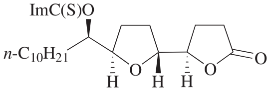
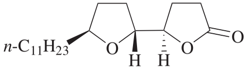
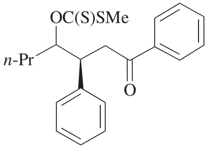
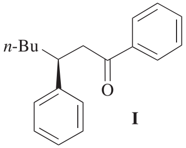
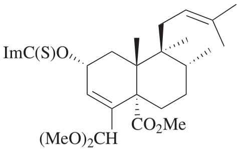
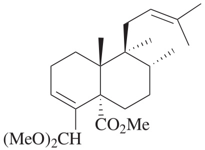
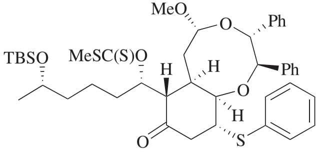
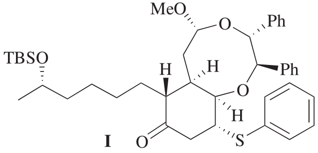
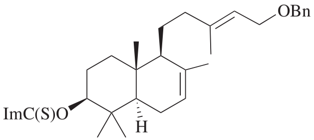
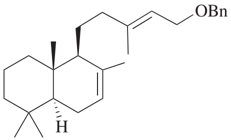
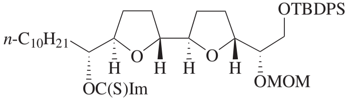
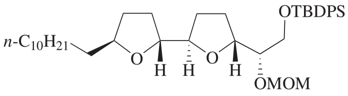
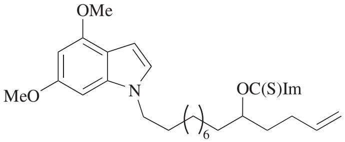
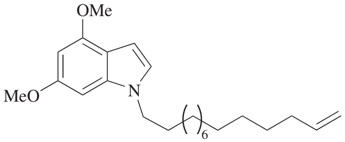
		(TMS)$_3$SiH, AIBN, toluene, sealed tube, 125°	 **I** (99)	914
		(TMS)$_3$SiH, AIBN, toluene, sealed tube, 125°	**I** (40) +  (56)	914
C$_{19}$		(TMS)$_3$SiH, AIBN, toluene, sealed tube, 125°	 **I** (99)	914
		(TMS)$_3$SiH, AIBN, toluene, sealed tube, 125°	**I** (31) +  (66)	914
		Bu$_3$SnH, AIBN, toluene, 90°, 3 h	 (91)	1087
		Bu$_3$SnH, Et$_3$B, benzene, rt, 0.5 h	 **I** (6)	1088
		(TMS)$_3$SiH, AIBN, toluene, 85–105°, 2 h	**I** (22)	1088

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	Bu_3SnH, AIBN, benzene, reflux	 (93)[c]	1089
	Bu_3SnH (2 eq), AIBN (0.2 eq), PhSH (0.2 eq), benzene, reflux, 5 h	 **I** (60)	1090
	$(TMS)_3SiH$, ACVA (1 eq), additive (0.2 eq), $EtOH–H_2O$ (99.5:0.5), 70°	**I** Additive — **I** none — (75) PhSH — (94) PhSSPh — (90)	1090
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (67)	1091
C_{21}			
	Bu_3SnH, AIBN, toluene, rt, 2 h	 (65)	1092
C_{22}			
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (84)	1093

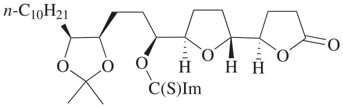
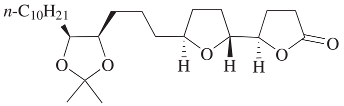
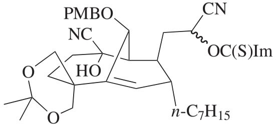
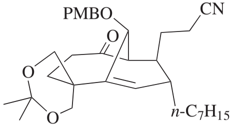
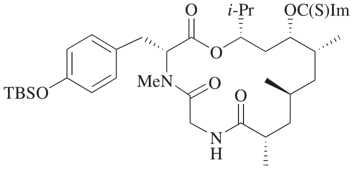
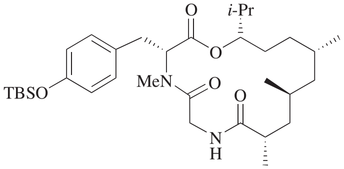
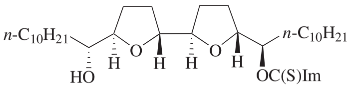
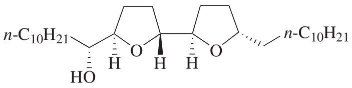
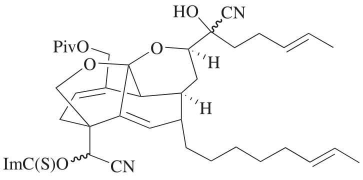
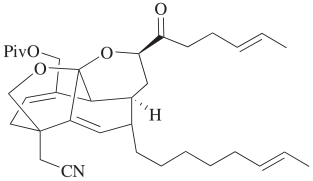
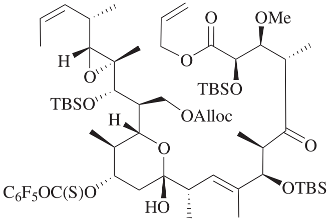
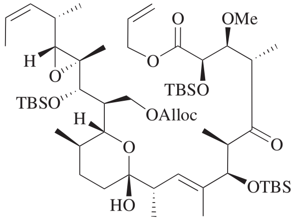
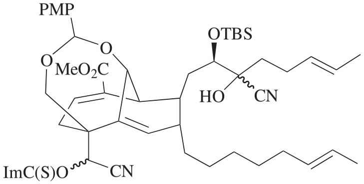
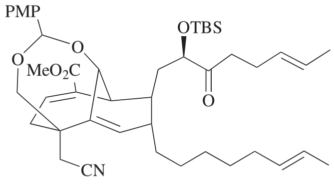
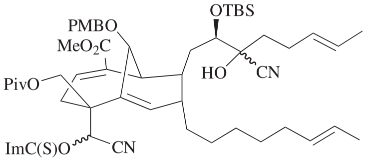
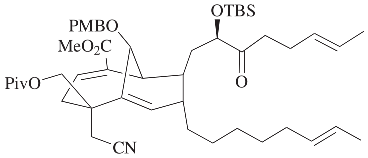
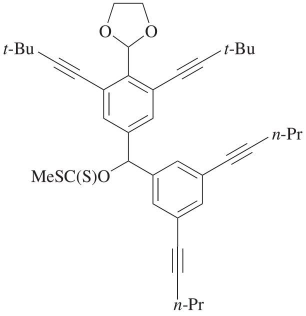
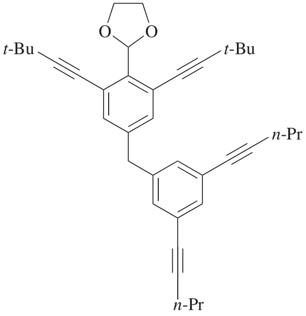
C_{23}		Bu_3SnH, AIBN, toluene, 90°, 3 h		(70)	1087
C_{22}		Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 0.5 h		(66)^c	27
C_{26}		Bu_3SnH, toluene, reflux, 5 min		(85)	810
C_{30}		Bu_3SnH, AIBN, toluene, 50°, 1.5 h		(66)	1094
		Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 0.5 h		(82)^c	27

TABLE 2F. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{31}			
	Bu_3SnH, Et_3B	 (50)[b]	1095
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 0.5 h	 (78)[c]	27
	Bu_3SnH, AIBN, CH_2Cl_2, sunlamp, 20°, 0.5 h	 (73)[c]	27

C_{36}		Bu_3SnH, AIBN, 80°, 10 h	 (43)	1096

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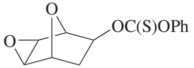
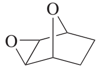
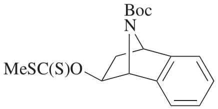
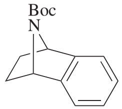
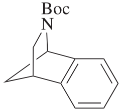
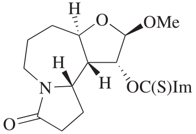
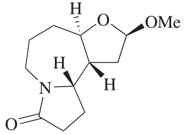
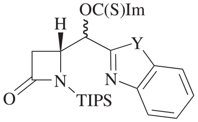
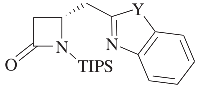
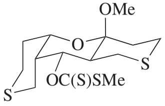
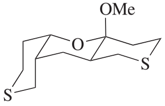
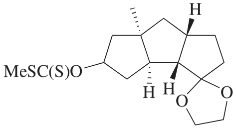
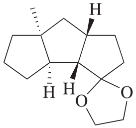
[a] The yield is based on reacted starting material.

[b] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[c] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (18)	1097
C_{10}			
	$(TMS)_3SiH$, AIBN, toluene, reflux, 2 h	 **I** +  **II** **I** + **II** (—), **I**:**II** = 1:1	144
	$(TMS)_3SiH$ (added slowly), AIBN, toluene, reflux, 2 h	**II** (90%)	144
C_{11}			
	Bu_3SnH, AIBN, toluene, reflux, 12 h	 $(45)^a$	1098
	Ph_3SnH, AIBN, benzene, reflux, 45 min	 Y: NSEM (82); S (71)	159
	Bu_3SnH, AIBN, toluene, reflux	 (91–97)	1099
C_{12}			
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (76)	1100

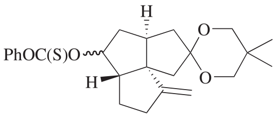
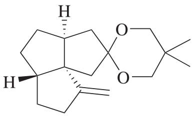
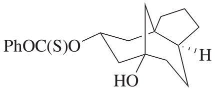
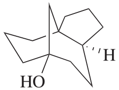
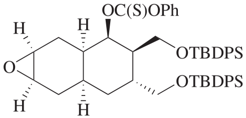
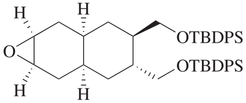
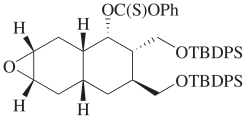
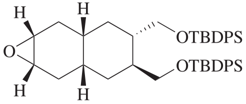
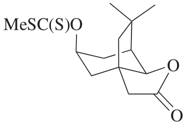
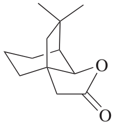
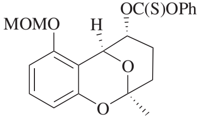
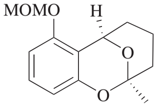
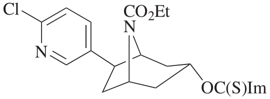
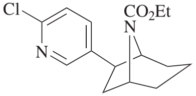
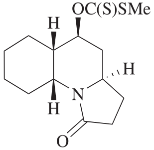
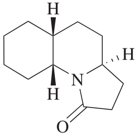
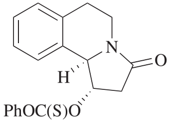
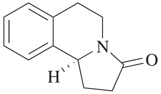
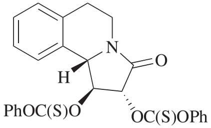
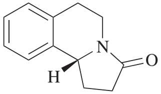
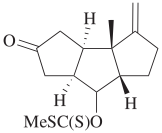
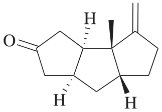
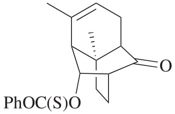
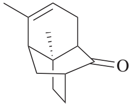
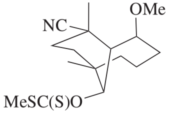
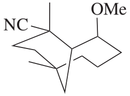
	Bu$_3$SnH, AIBN, benzene, reflux		(60)[b]	1101
	Bu$_3$SnH, AIBN, toluene, reflux, 3 h		(100)	1102
 racemic	Bu$_3$SnH, AIBN, toluene, 90°, 1 h		(82)	1103
 nonracemic	Bu$_3$SnH, AIBN, toluene, 90°, 0.5 h		(96)	1104
	Bu$_3$SnH, AIBN, benzene, reflux, 4 h		(—)	1105
	Bu$_3$SnH		(56)[a]	1106
	Bu$_3$SnH, AIBN, toluene, reflux		(73)	1107

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}		Bu_3SnH, toluene, reflux, 4 h		(93)	1108
		Bu_3SnH, AIBN, toluene, reflux, 5 h		(51)	243
		Bu_3SnH, AIBN, toluene, reflux, 5 h		(49)	243
C_{13}		Bu_3SnH, AIBN, toluene		(—)	1109
		$(TMS)_3SiH$, AIBN, benzene, reflux, 1.5 h		(88)	180
		Bu_3SnH, toluene, reflux		$(43)^b$	1020

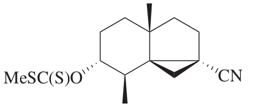
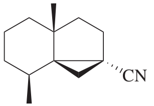
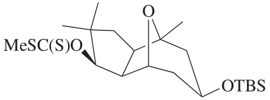
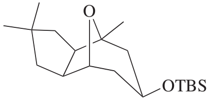
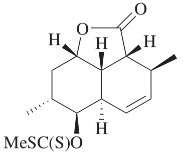
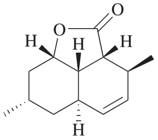
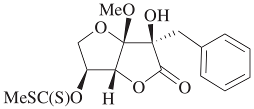
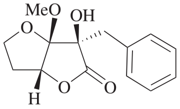
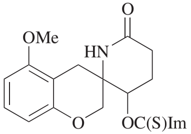
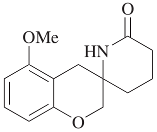
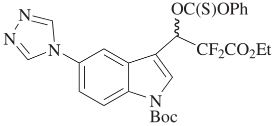
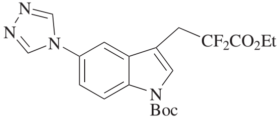
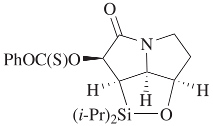
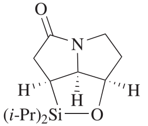
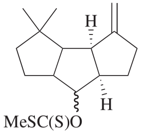
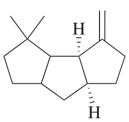
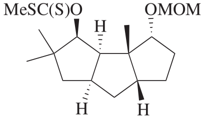
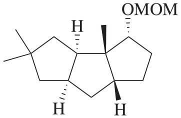
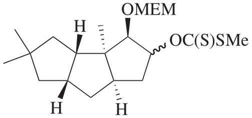
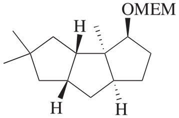
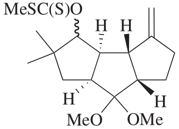
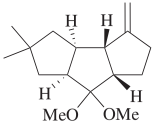
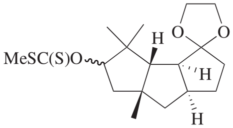
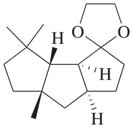
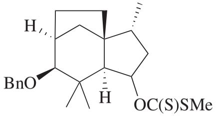
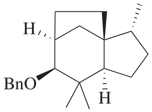
C_{13}				
	Bu_3SnH, AIBN, THF reflux		(75)[a]	1110
	Bu_3SnH, AIBN, toluene, reflux, 6 h		(50)	1111
	Bu_3SnH, AIBN, toluene, reflux, 35 min		(68)[a]	1112
	Bu_3SnH, toluene, reflux, o/n		(87)	1113
	Bu_3SnH, AIBN, toluene–THF, reflux		(94)	1114
	Bu_3SnH, AIBN, toluene, reflux, 2.5 h		(43)[b]	1115
	Bu_3SnH, AIBN, toluene, 100°, 4.5 h		(84)	1116

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (64)	1117
	Bu_3SnH, toluene, reflux	 (90)	1118
	Bu_3SnH, AIBN, toluene, 100°, 17 h	 (92)	1119
	Bu_3SnH, AIBN, toluene, reflux, 10 min	 (80)	1120
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (76)	1100
	Bu_3SnH, AIBN, toluene, reflux, 11 h	 (91)	1121

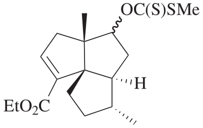
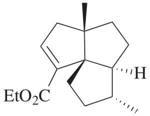
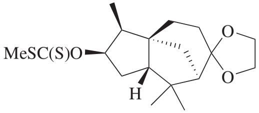
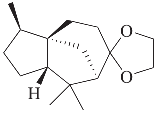
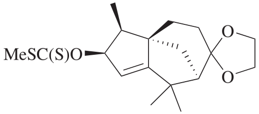
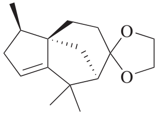
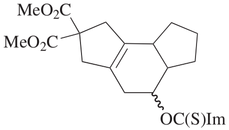
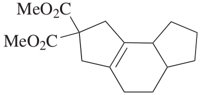
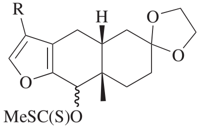
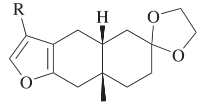
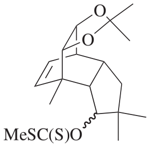
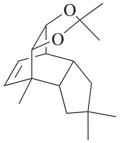
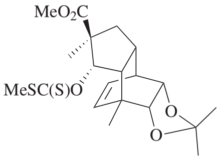
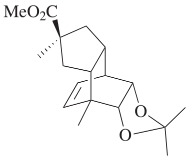
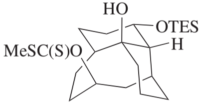
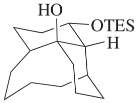
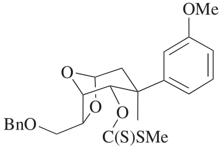
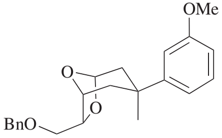
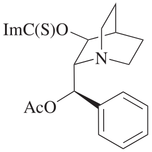
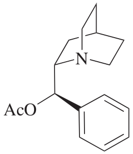
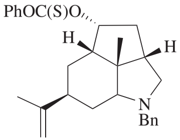
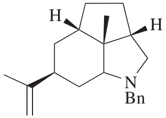
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (70)	1122
	Bu_3SnH, AIBN, benzene, reflux	 (76)	1123
	Bu_3SnH, AIBN, benzene, reflux, 2 d	 (76)	1124
	Bu_3SnH, AIBN	 (79)	1125
C_{14-16}			
	Bu_3SnH, AIBN, toluene, reflux, 72 h	 R Me (47)[b] TMS (22)[b]	1126
C_{14}			
	Bu_3SnH, AIBN, toluene, 100°, 17 h	 (57)	1119

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 (97)	1127, 1128
	Bu_3SnH, AIBN, benzene, reflux, 0.25 h	 (87)[a]	1129
	Bu_3SnH, AIBN, benzene, reflux	 (95)	1130
	Bu_3SnH, toluene, reflux, 3.75 h	 (88)	1131
	Bu_3SnH, AIBN, toluene, 75°, 1.5 h	 (67)	1132

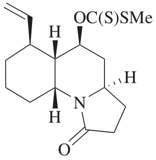
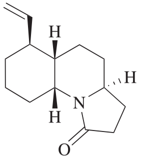
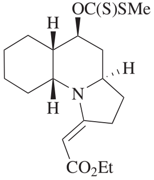
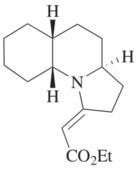
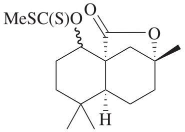
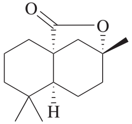
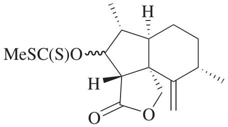
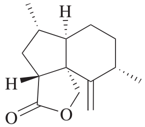
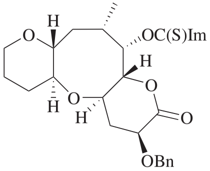
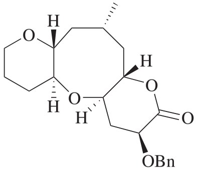
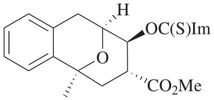
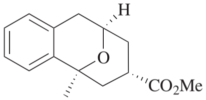
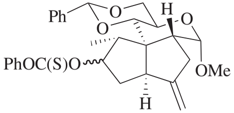
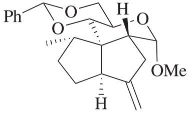
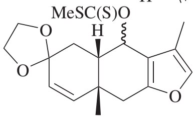
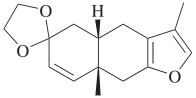
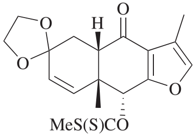
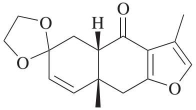
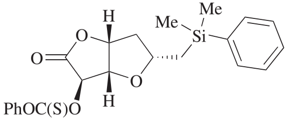
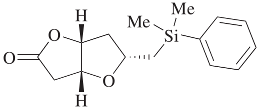
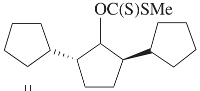
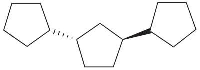
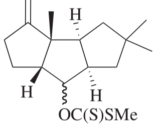
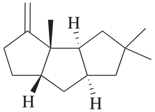
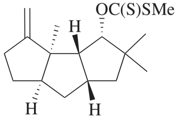
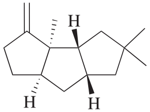
	Bu_3SnH, toluene, reflux, 4 h		(68)	1133, 1134
	Bu_3SnH, toluene, ia, reflux, 6.5 h		(98)	1108
	Bu_3SnH, AIBN, benzene, reflux, 10 h		(95)	1042
	Bu_3SnH, Et_3B, toluene, 0°		(67)	1135
	Bu_3SnH, toluene, reflux, 40 min		(88)	254
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h		(63)	1136

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	Bu_3SnH	 $(70)^b$	1137
	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 (>90)	1138
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 (95)	1138
C_{15} 	Bu_3SnH, toluene, reflux, 3 d	 (96)	1139
	Ph_3SnH, AIBN, toluene, reflux, 5.5 h	 (73)	257
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 $(70)^b$	1140, 1141
	Bu_3SnH, toluene, reflux	 (19)	1142

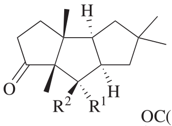
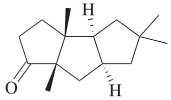
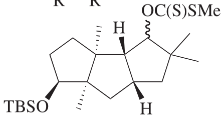
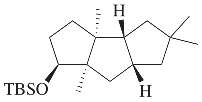
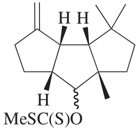
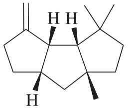
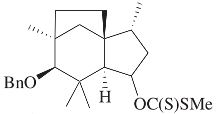
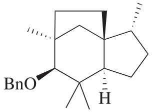
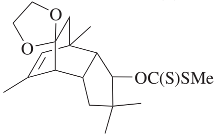
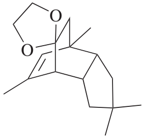
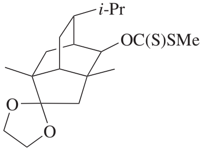
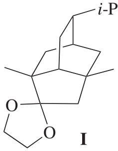
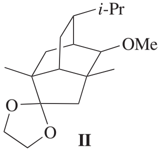
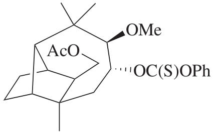
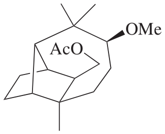
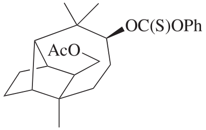
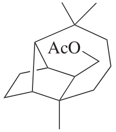
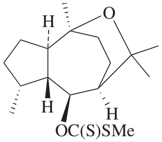
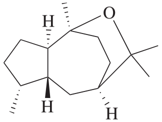
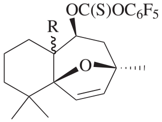
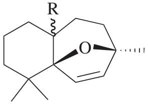
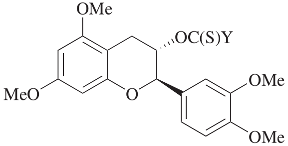
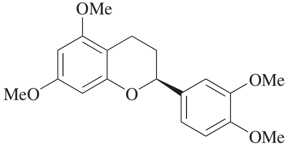
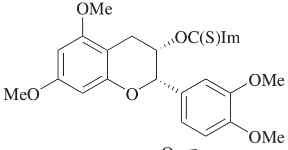
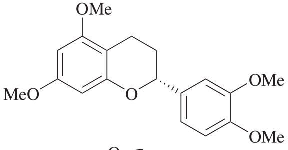
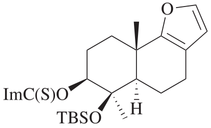
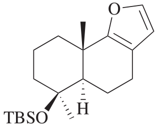
	Bu$_3$SnH, Et$_3$B, O$_2$, hexane, 0°, 1 h	 R^1 R^2 PhOC(S)O H (72) H PhOC(S)O (73)	1143
	Bu$_3$SnH, AIBN, toluene, reflux, 0.5 h	 (64)^b	1144
	Bu$_3$SnH, AIBN, toluene, reflux, 6 h	 (64)^a	1117
	Bu$_3$SnH, AIBN, toluene, reflux, 11 h	 (94)	1145
	Bu$_3$SnH, toluene, reflux, 12 h	 (52)	1146
	Bu$_3$SnH, AIBN, solvent, reflux	 **I** +  **II** [M]^c Solvent **I + II** **I:II** 0.027 benzene (91)^a 3:2 0.008 benzene (—) 4:1 — toluene **I** (73)^a —	1036
	Bu$_3$SnH, AIBN, toluene, 110°, 4 h	 (71)^b	1147

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		Bu_3SnH, AIBN, toluene, 110°, 4 h	 $(50)^b$	1147
		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (98)	1148
		PMHS, $(Bu_3Sn)_2O$ (cat.), AIBN, BuOH, toluene, reflux	 R α-Me (89) β-Me (71)	153
		Bu_3SnH, AIBN, toluene, reflux, 3 h	 Y Im (85) OPh (81) SMe (72)	1149
		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (77)	1149
		Bu_3SnH, AIBN, xylene, reflux, 4.5 h	 (85)	1150

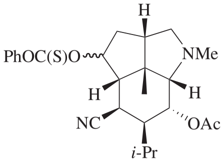
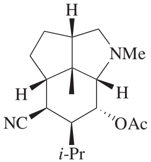
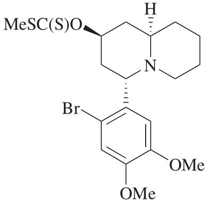
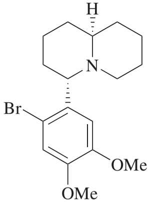
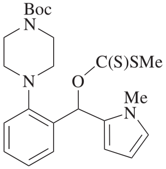
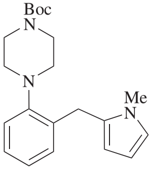
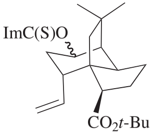
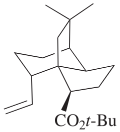
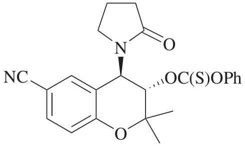
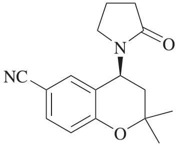
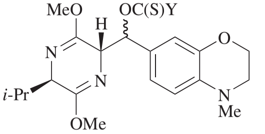
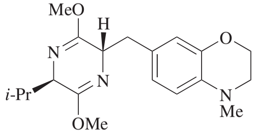
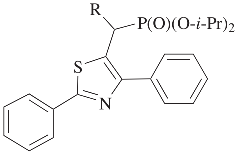
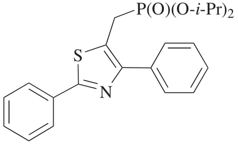
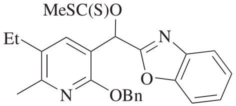
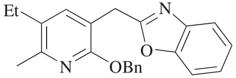
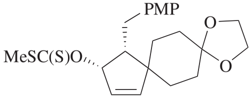
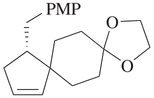
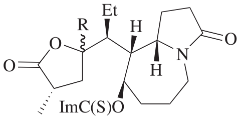
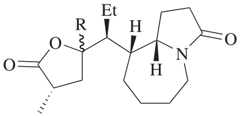
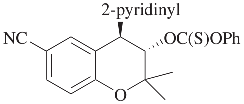
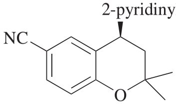
		Bu$_3$SnH, AIBN, toluene		(83)	1151
		Bu$_3$SnH, AIBN, toluene, 80°, 2 h		(47)	1134
		Bu$_3$SnH, AIBN, toluene, 80°, 16 h		(66)	1152
C$_{16}$		Bu$_3$SnH, toluene, reflux		(66)^b	1153
		Bu$_3$SnH, AIBN, toluene		(13)^a	1154

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	Bu_3SnH, AIBN	 Y SMe (60) OPh (—)	1155
	Bu_3SnH, AIBN, toluene, 80°	 R PMPOC(S)O (90) PMPOC(O)S (98)	960
	Bu_3SnH, AIBN, toluene, reflux, 16 h	 (25)[a]	1156
C_{17} 	Bu_3SnH, AIBN, benzene, reflux, 1.5 h	 (80)	1157
	Bu_3SnH, toluene, 5 h	 R α-H (59) β-H (65)	1158
	Bu_3SnH, AIBN, toluene	 (28)[a]	1154

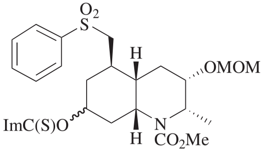
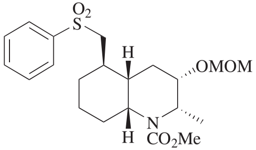
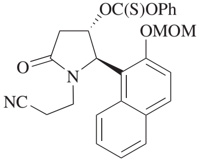
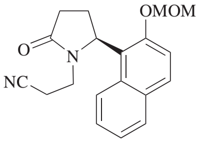
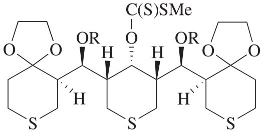
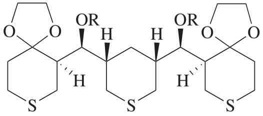
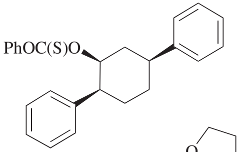
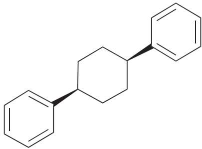
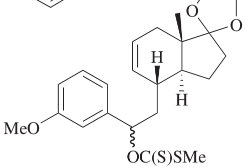
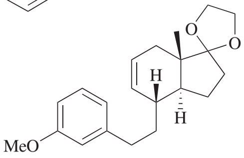
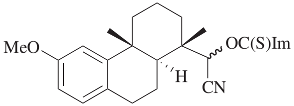
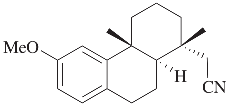
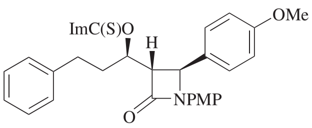
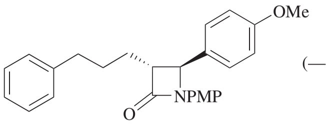
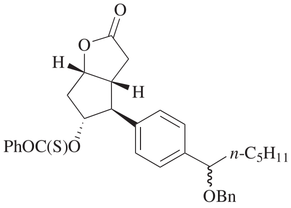
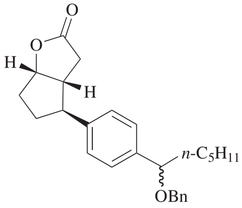
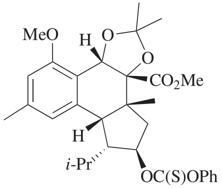
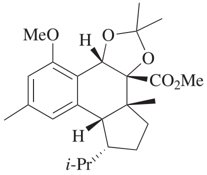
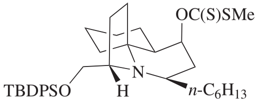
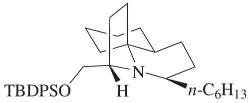
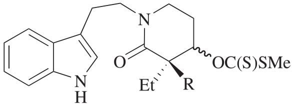
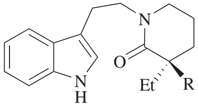
		Bu$_3$SnH, toluene, reflux, 3 h		(84)	1159
		Bu$_3$SnH, AIBN, benzene, reflux, 1.5 h		(95)	1160
	 R = MOM	Bu$_3$SnH, AIBN		(40)^b	1161
C$_{18}$		Bu$_3$SnH, AIBN, toluene, reflux, 13 h		(53)	1162
		Bu$_3$SnH, AIBN, toluene, reflux		(86)^a	1163
		Bu$_3$SnH, AIBN, CH$_2$Cl$_2$, sunlamp, 20°, 30 min		(88)^b	27

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}			
	Bu_3SnH, AIBN, DMSO, 90°, 4 h	 (—)	1164
C_{19}			
	$(TMS)_3SiH$, AIBN	 (60)[b]	1165
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (75)	1166
	Bu_3SnH, AIBN, benzene	 (79)[b]	1167
C_{19-20}			
	Bu_3SnH, AIBN, toluene, reflux	 R Et (73) $(CH_2)_3OTBDPS$ (85)	1168

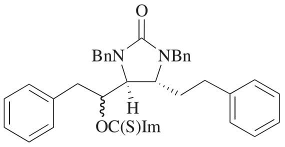
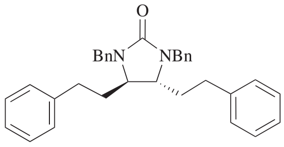
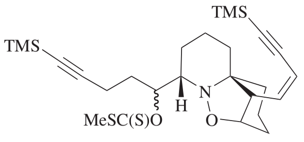
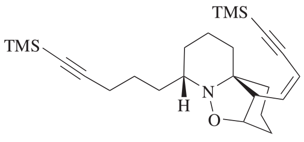
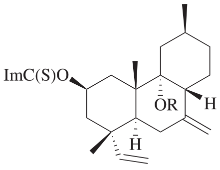
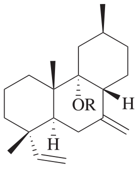
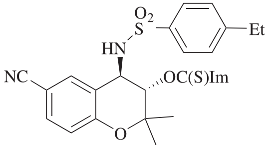
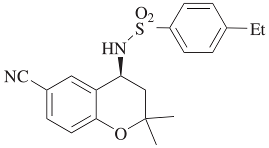
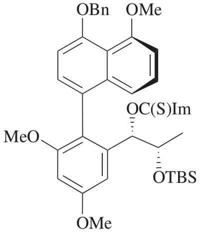
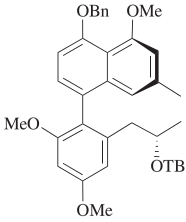
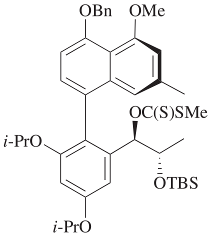
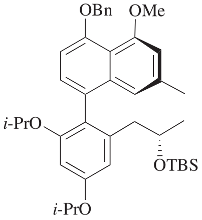
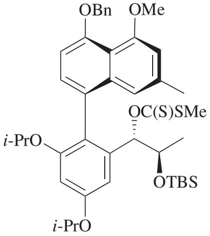
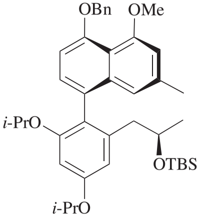
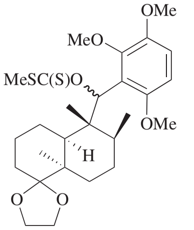
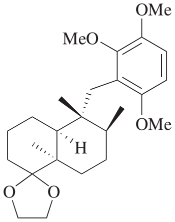
C_{19}		Bu_3SnH		(—)	1169
		Bu_3SnH, AIBN, benzene, reflux		(70)	101
C_{20}	 R = TMS	Ph_3SnH, AIBN, benzene, reflux		(74)	1170
		Bu_3SnH, AIBN, toluene		$(33)^b$	258
		Bu_3SnH, AIBN, toluene, rt, 53 h		$(62)^a$	1171, 1172

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	Bu_3SnH, AIBN, toluene, 100°, 0.25 h	 (94)	1173
	Bu_3SnH, AIBN, toluene, 100°, 0.25 h	 (99)	1173
	Bu_3SnH, AIBN, toluene, reflux	 (77)	1174

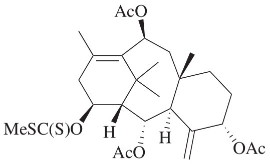
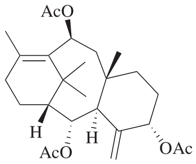
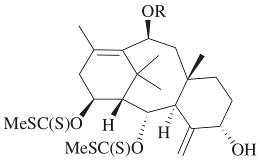
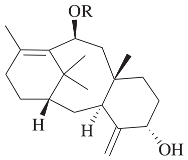
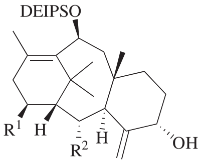
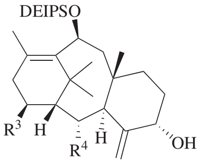
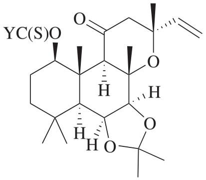
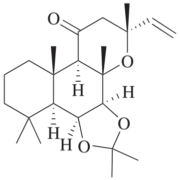
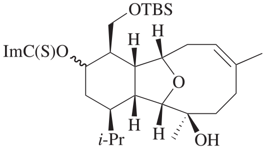
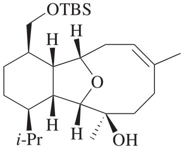
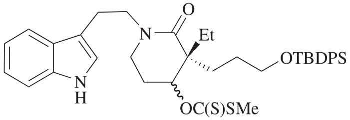
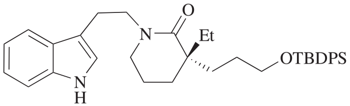
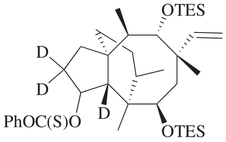
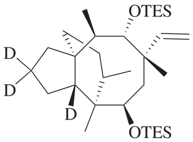
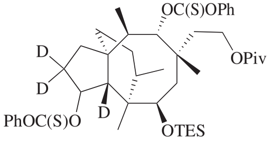
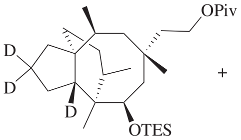
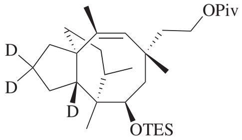
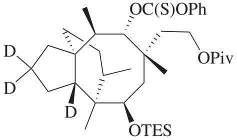
	Bu_3SnH, AIBN, toluene, 80°	 **I** (80)	1175, 1176, 1177
	H_3PO_2, AIBN, dioxane, reflux	**I** (82)	1178
	H_3PO_2, AIBN, Et_3N, cyclohexene, dioxane, reflux, 0.5 h	**I** (74)	1178
	Bu_3SnH, AIBN, toluene, reflux	 R TBS (73) DEIPS (46)	1179
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 R^1 R^2 R^3 R^4 PhOC(S)O OH H OH (52) OH PhOC(S)O OH H (59) PhOC(S)O PhOC(S)O H H (52)	1180 1180 1180, 1179
	Bu_3SnH, AIBN, toluene, 100–120°, 0.5–0.75 h	 Y MeS (72) Im (82) PhO (41)	1181, 1182

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	Bu_3SnH, AIBN, toluene, 100°	 (72)[b]	1183
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (85)	1168
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (63)[b]	1184
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 **I** +  **II** **I** + **II** (—), **I**:**II** = 1:1.9	1184
	Bu_3SnH, Et_3B, benzene, 0°, 3 h	**I** + **II** (32), **I**:**II** = 4:1 +  (24)	1184

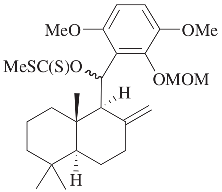
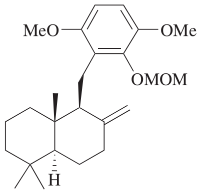
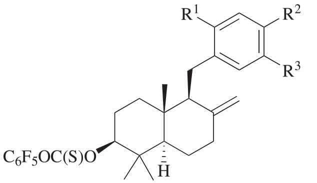
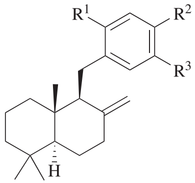
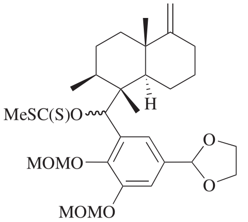
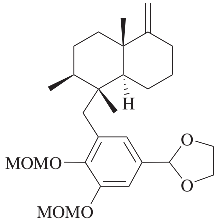
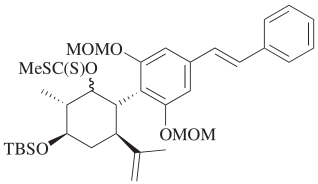
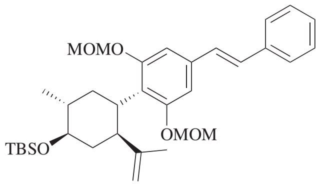
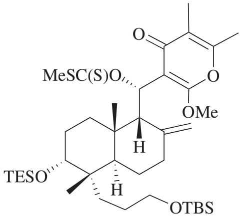
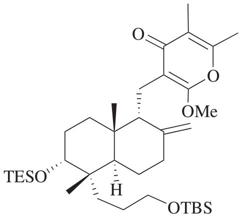
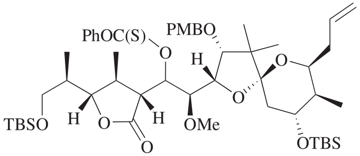
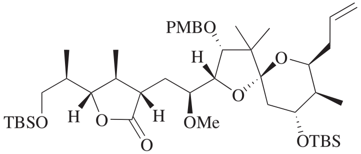
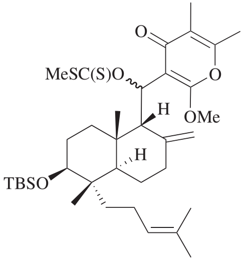
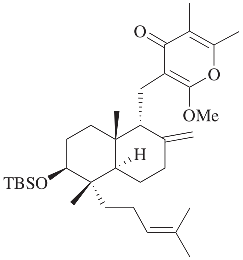
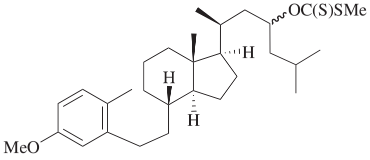
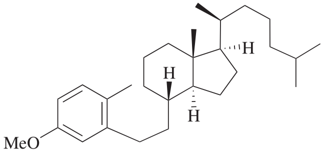
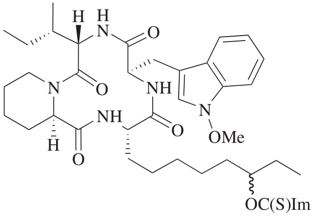
C_{21}			
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (92)[a]	1185
	Bu_3SnH, AIBN, benzene, reflux	 R^1 R^2 R^3 H —OCH_2O— (87) OMe H OMe (89)	1069, 1186
C_{22}			
	Bu_3SnH, AIBN, toluene, reflux	 (92)	1187
C_{24}			
	Bu_3SnH, AIBN, toluene, 90°, 0.5 h	 (91)	1187a

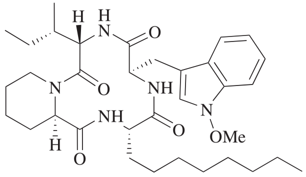
TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24}			
	Bu_3SnH, AIBN, toluene, reflux	 (77)	1188
	Bu_3SnH, AIBN, 100°	 (75)	1189
C_{27}			
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (92)	1190
	Bu_3SnH, AIBN, toluene, reflux, 40 h	 (95)	60

C_{33}

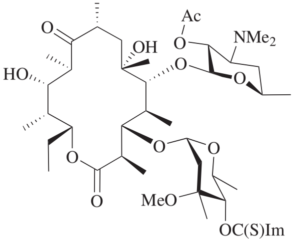


Bu_3SnH, AIBN, toluene, reflux

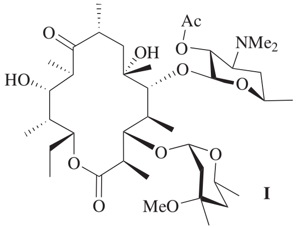


(74) 1191

C_{34}



NaH_2PO_2 (5 eq), ACVA (*x* eq), phase-transfer agent (PTA), solvent, reflux



I

Solvent	PTA	*x*	Time (min)	
EtOH	TBAH[d]	0.7	120	(71)
n-PrOH	TBAH[d]	0.7	50	(94)
i-PrOH	TBAH[d]	0.7	120	(92)
2-ME	none	0.7	20	(80)
2-ME	TBAH[d]	0.7	10	(95)
n-PrOH	TBPB[e]	0.7	60	(90)
2-ME	Et_3N[d]	1.0	40	(83)

203

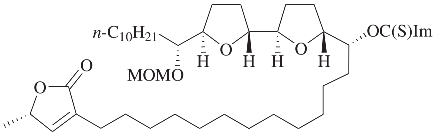
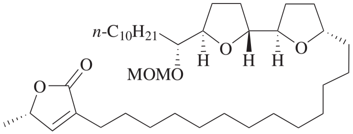
NaH_2PO_2 (10 eq), initiator (1 eq), TBPB (1 eq), Et_3N (pH 8.0), 2-ME, reflux

I

Initiator	Time (min)	**I**
ACVA	20	(95)
AMHP	60	(86)

203

TABLE 2G. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{37}			
	Bu_3SnH, AIBN, toluene, rt, 2 h	 (54)[b]	1092

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[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

[c] This value is the initial molarity of the starting material.

[d] The basic reagents (TBAH or Et_3N) were added to pH 7–8.

[e] One equivalent of TBPB was used.

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES

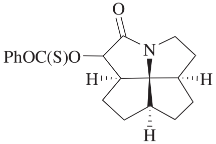
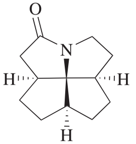
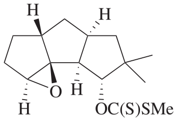
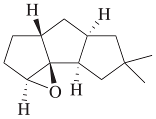
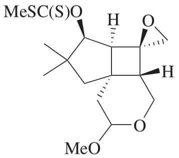
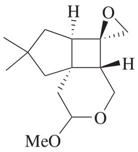
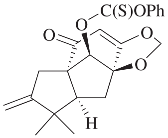
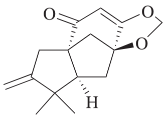
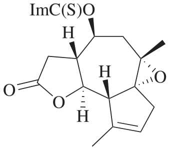
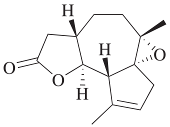
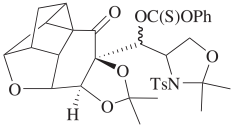
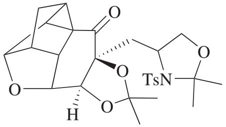
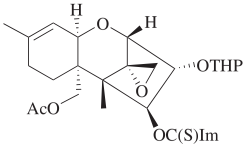
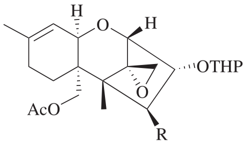
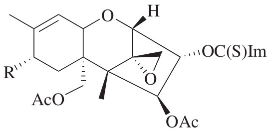
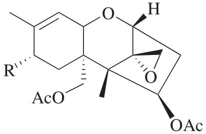
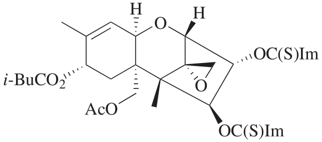
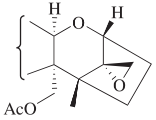
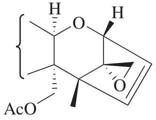
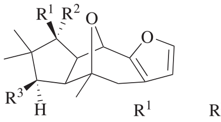
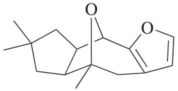
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	Bu_3SnH, AIBN, benzene, reflux	 (98)	255, 256
C_{13} 	Bu_3SnH, toluene, reflux, 24 h	 (60)[a]	1192
	Bu_3SnH, toluene, reflux	 (73)[a]	1193
C_{14} 	Bu_3SnH, AIBN, benzene, reflux, 18 h	 (42)	1194
	Bu_3SnH, AIBN, toluene, 90°, 5 h	 (77)	1195

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}		Bu_3SnH, Et_3B, toluene, rt, 1 h	 (95)	1196, 1197
C_{15}		Bu_3SnR, AIBN, toluene	 R Temp Time (h) H reflux 2.5 (>90) D 80° 0.5 (84)	271 272
		Bu_3SnH, AIBN, solvent, reflux	 Solvent R benzene H (85) toluene i-$BuCO_2$ (62)	270 241
		Bu_3SnH, toluene, reflux	 (31) +  (—)	241
	 R^1 R^2 R^3 OC(S)Im H H H OC(S)Im H H H OC(S)Im	Bu_3SnH, toluene, reflux, 0.5 h	 (71)[a]	1198

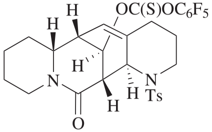
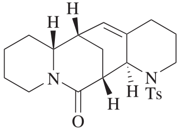
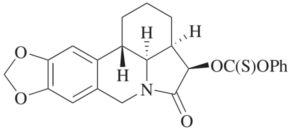
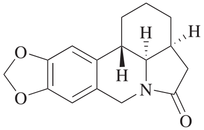
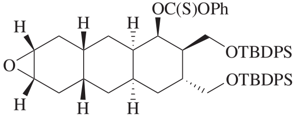
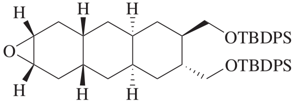
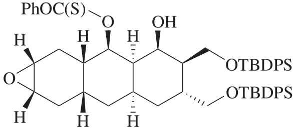
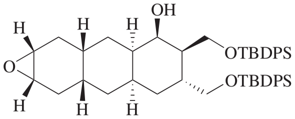
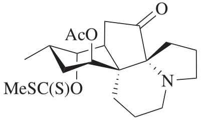
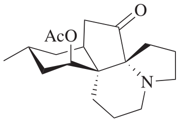
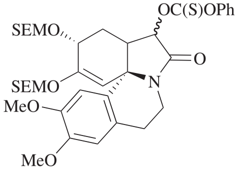
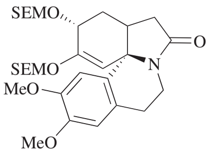
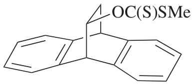
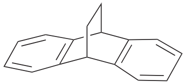
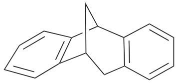
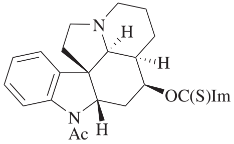
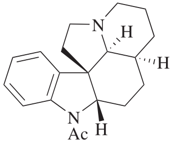
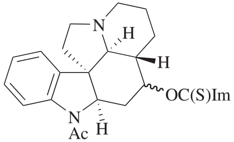
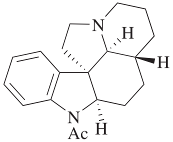
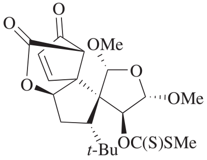
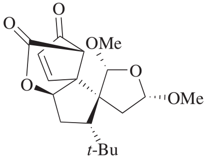
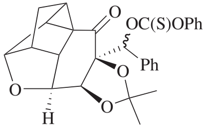
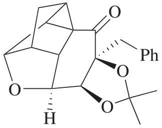
		Bu_3SnH, AIBN, benzene, reflux, 1 h		(70)[a]	1199
		Bu_3SnH, AIBN, benzene, reflux, 22 h		(72)	99
C_{16}		Bu_3SnH, AIBN, toluene, 90°, 15 min		(99)	1200
		Bu_3SnH, AIBN, toluene, 90°, 15 min		(97)	1200
		Bu_3SnH, AIBN, toluene, reflux		(77)	1201
		Bu_3SnH, AIBN		(83)[b]	1202

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}		Bu_3SnH	 **I** +  **II** **I** + **II** (—), **I**:**II** = 68:32	1203
C_{17}		Bu_3SnH, xylenes, reflux, 2 h	 (93)	1204
		Bu_3SnH, xylenes, reflux, 2 h	 (71)	1204
		Bu_3SnH, AIBN, benzene	 (75)	1205
C_{18}		Bu_3SnH, AIBN, toluene, reflux, 2 h	 (79)	1197, 1206

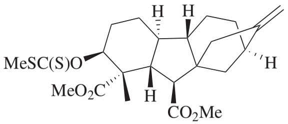
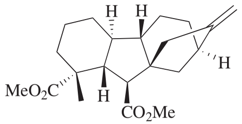
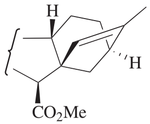
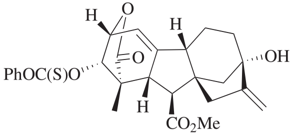
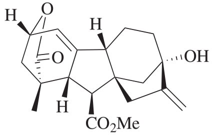
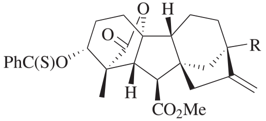
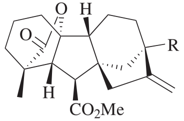
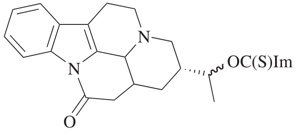
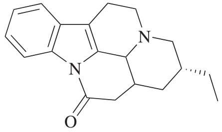
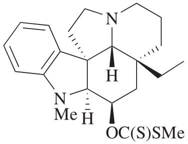
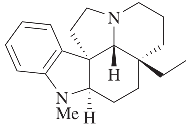
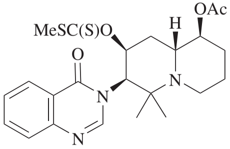
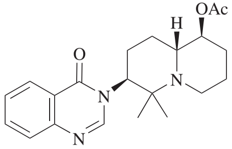
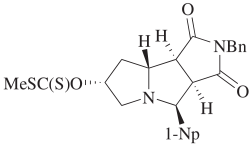
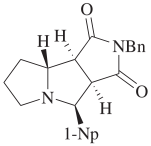
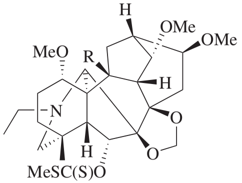
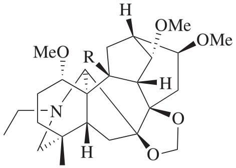
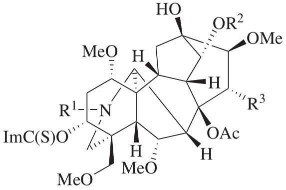
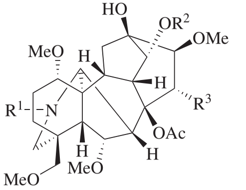
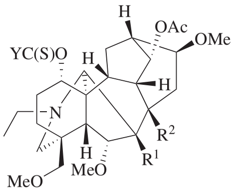
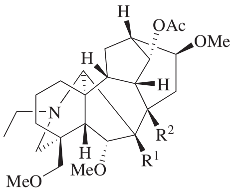
C_{19}		Bu_3SnH, AIBN, benzene, reflux 2.5 h	 **I** +  **II** **I** + **II** (55), **I**:**II** = 1:1		1207
		Bu_3SnH, AIBN, solvent, reflux, 35 min		(74)	1208
		Bu_3SnH, ia, toluene, reflux		R Time (h) H 2 (87) OAc 1.5 (90)	1209
		Bu_3SnH, toluene, reflux, 3.5 h		(57)[a]	1210
		Bu_3SnH, AIBN, toluene, reflux, 1 h		(96)	1211
		Bu_3SnH, AIBN, toluene, reflux, 2 h		(81)[a]	1212

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (88)	1213
	Bu_3SnH, AIBN, benzene, reflux	 R OH (74) H (78)	1214
	Bu_3SnH, AIBN, solvent, 80°	 R^1 R^2 R^3 Solvent Et Ac H benzene (85) Me Bz OH benzene (92) Et Bz OH benzene (86) Et Bz OH toluene (76)	1214 1214 1214 1215
	Bu_3SnH, AIBN, benzene, reflux	 Y R^1 R^2 PhO H OAc (97) Im OH OH (87)	1214

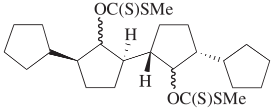
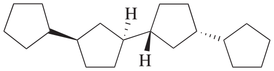
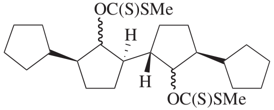
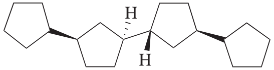
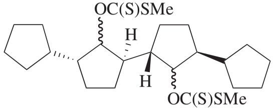
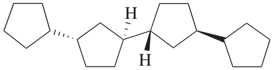
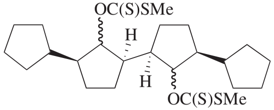
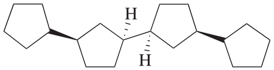
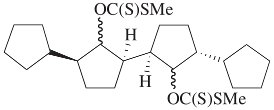
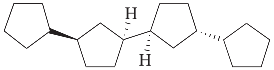
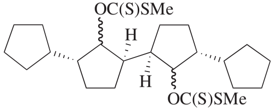
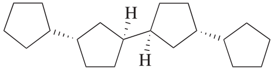
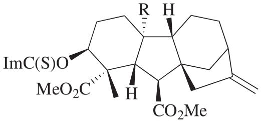
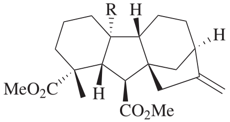
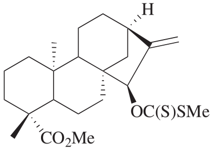
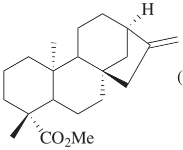
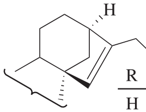
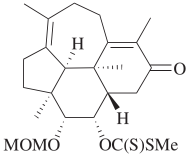
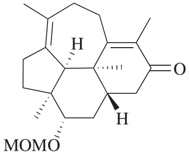
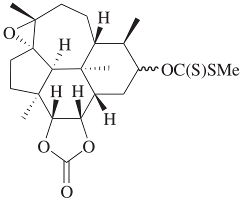
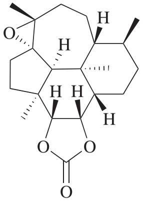
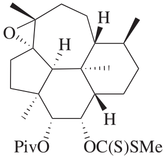
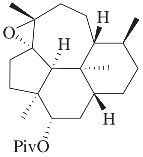
C_{20} 	Ph_3SnH, AIBN, toluene, reflux, 4 h		(30)	257
	Ph_3SnH, AIBN, toluene, reflux, 4 h		(32)	257
	Ph_3SnH, AIBN, toluene, reflux, 4 h		(—)	257
	Ph_3SnH, AIBN, toluene, reflux, 4 h		(—)	257
	Ph_3SnH, AIBN, toluene, reflux, 4 h		(—)	257
	Ph_3SnH, AIBN, toluene, reflux, 4 h		(—)	257

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	Bu_3SnH, AIBN, benzene, reflux, 4 h	 R CO_2Me (87) Me (87)	1216
	Bu_3SnH, toluene, reflux, 2 h	 (43) +  R H (44) SC(O)SMe (10)	50
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (55)	1217
	Ph_3SnH, AIBN, toluene, reflux, 1 h	 (61)	1217
	Ph_3SnH, AIBN, toluene, reflux, 3 h	 (100)	1217

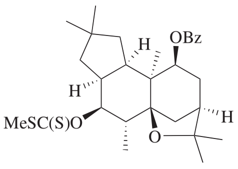
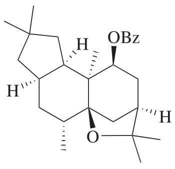
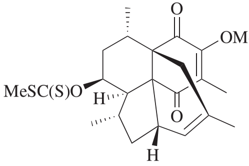
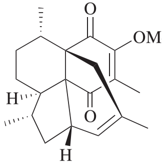
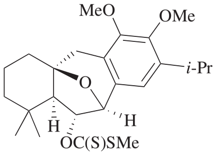
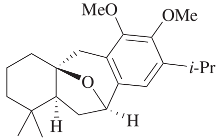
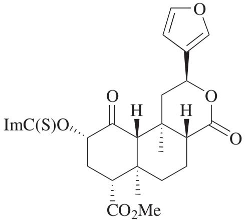
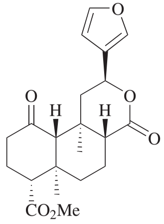
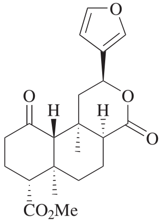
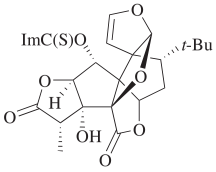
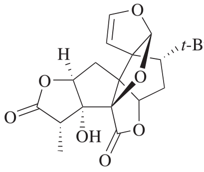
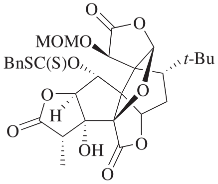
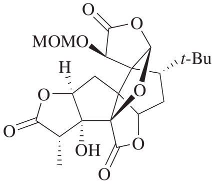
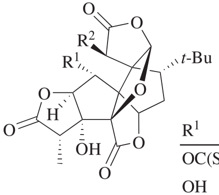
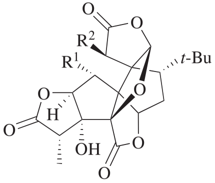
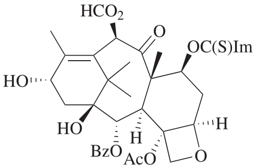
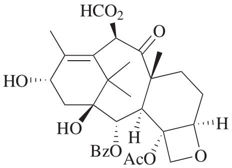
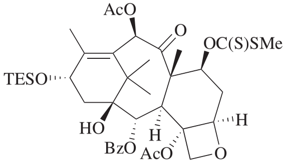
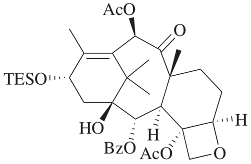
	Bu_3SnH, toluene, reflux, 20 h	 (95)	1218, 1219
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (88)	1220, 1221
	Bu_3SnH, AIBN, heat	 (67)[a]	1222
	Bu_3SnH, AIBN, toluene, reflux, o/n	 (28) +  (13)	1223
	Bu_3SnH, dioxane, reflux	 (90)	63

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	Bu_3SnH, dioxane, reflux	 (71)	63
 R¹ R² OC(S)OPh OH OH OC(S)OPh	Bu_3SnH, AIBN, toluene–EtOH, reflux, 5 h	 R¹ R² H OH (45)[a] OH H (54)[a]	1224
	Bu_3SnH, AIBN, dioxane, 80°	 (46)	1225
	Bu_3SnH, toluene, reflux	 (83)	1226

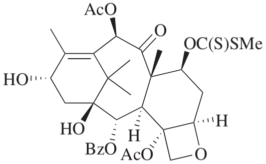
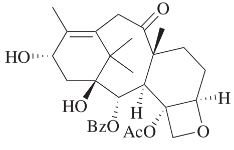
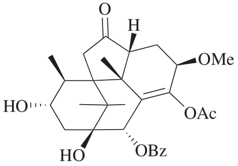
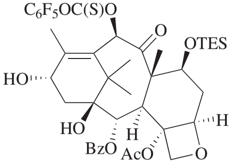
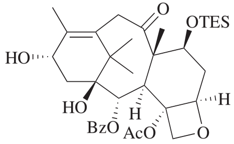
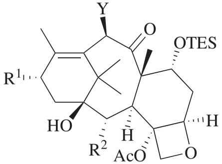
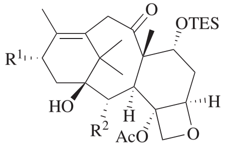
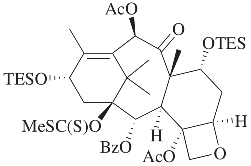
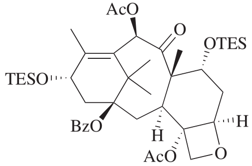
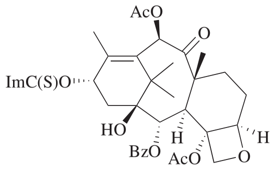
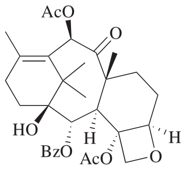
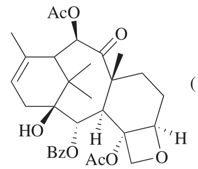
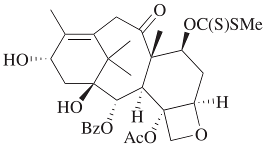
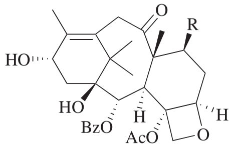
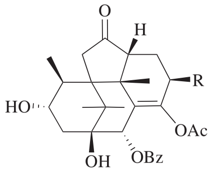
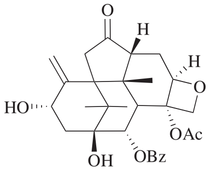
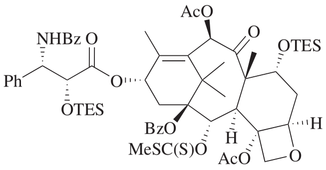
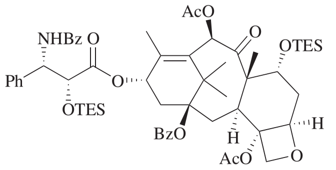
	Bu_3SnH, AIBN, toluene, 80°, 3 h	 (56) +  (22)	1226
	Bu_3SnH, AIBN, toluene, 90°, 1 h	 (99)	1226
 R¹ / R² / Y HO / OBz / $OC(S)OC_6F_5$ TESO / OC(S)SMe / H	Bu_3SnH, AIBN, toluene, 90°, 1–2 h	 R¹ / R² HO / OBz (99) TESO / H (80)	143
	Bu_3SnH, AIBN, toluene, 80°, 1 h	 (94)	143

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	Bu_3SnH, AIBN, toluene, 85°, 2 h	 (59) +  (17)	1227
	MH, AIBN, solvent, 80°	 **I** R = H, **III** R = OMe +  **II** R = OMe, **IV** R = H +  **V**	143

MH	Solvent	Time (h)	**I**	**II**	**III**	**IV**	**V**
Bu_3SnH	benzene	3	(52)	(25)	(—)	(—)	(—)
Ph_3SnH	benzene	2.5	(52)	(25)	(30)	(—)	(—)
$(TMS)_3SiH$	toluene	2.5	(—)	(19)	(—)	(19)	(2)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu_3SnH, AIBN, toluene, 90°, 1 h	 (72)[a]	151

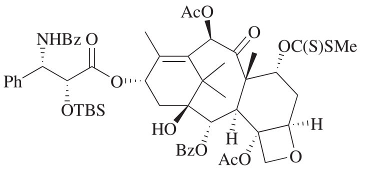
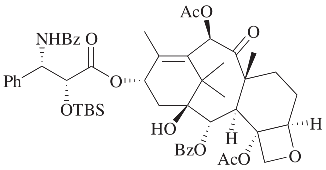
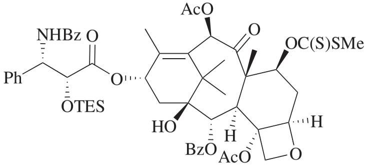
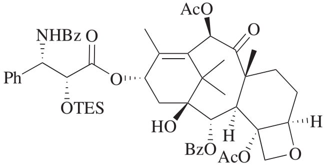
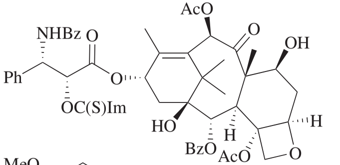
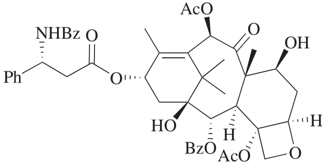
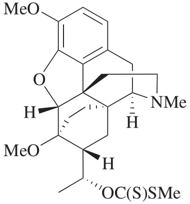
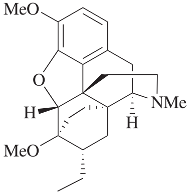
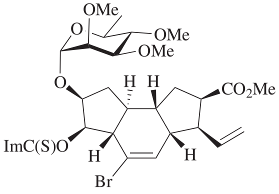
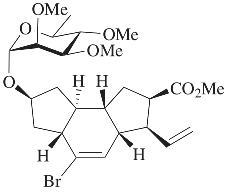
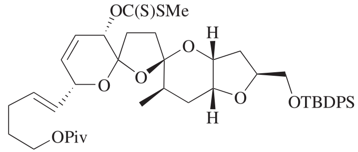
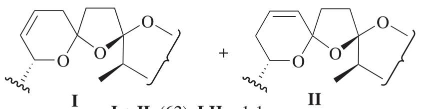
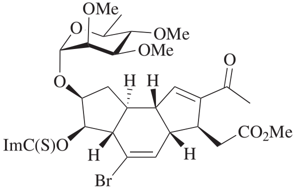
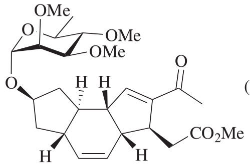
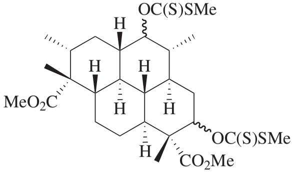
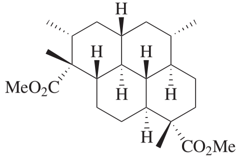
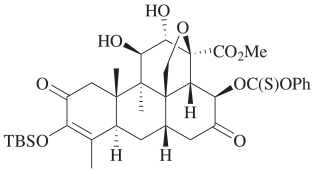
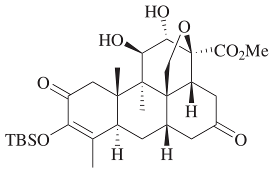
		Bu$_3$SnH, AIBN, toluene, 90°, 1 h		(48)^b	1226
		Bu$_3$SnH, AIBN, toluene, 75°		(49)^b	70
		Bu$_3$SnH, AIBN, toluene, 85°, 20 min		(80)	1229
		(Bu$_4$N)$_2$S$_2$O$_8$ (3 eq), HCO$_2$Na (6 eq), DMF, 65°, 0.25 h		(95)	211
C$_{21}$		Bu$_3$SnH, Et$_3$B, O$_2$, benzene, rt		(80)	249

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21} 	Bu_3SnH, AIBN, toluene, reflux, 1 h	 **I** + **II** (62), **I**:**II** = 1:1	1230
	Bu_3SnH, Et_3B, toluene, rt, 1 h	**I** + **II** (57), **I**:**II** = 1:1	1230
C_{22} 	$(TMS)_3SiH$, AIBN, dioxane, 80°	 (73)^b	1231
	Bu_3SnH, AIBN	 (47)^b	1232
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (65)	1233, 1234

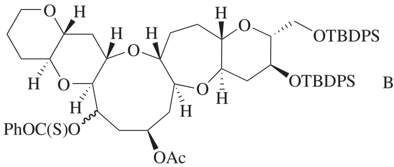
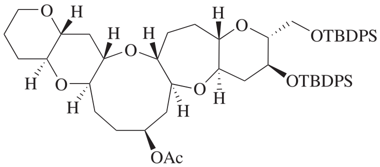
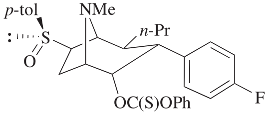
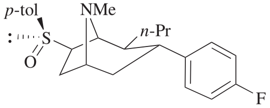
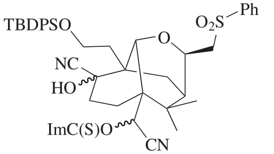
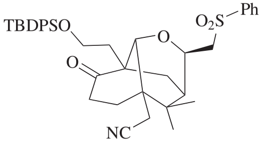
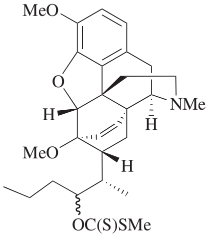
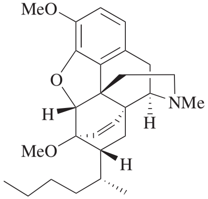
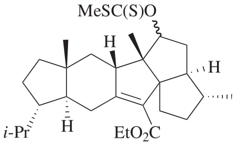
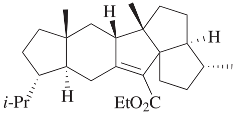
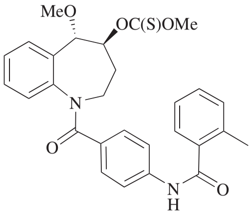
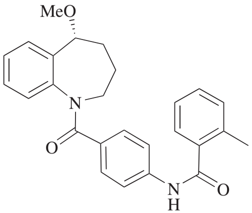
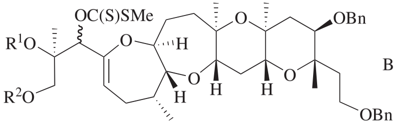
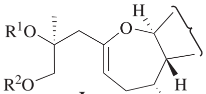
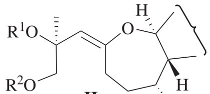
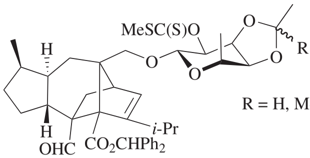
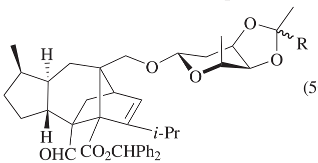
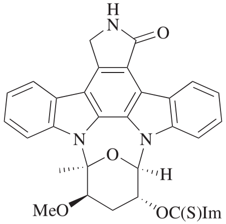
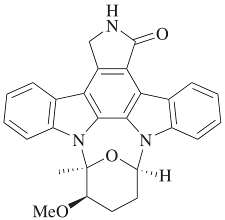
	Bu$_3$SnH, Et$_3$B, benzene, rt		(80)	253
	Bu$_3$SnH, AIBN, toluene, 60°		(50)^a	1235
C$_{24}$				
	Bu$_3$SnH, AIBN, CH$_2$Cl$_2$, sunlamp, 20°, 0.5 h		(80)^b	27
	Bu$_3$SnH, toluene, reflux, 3 h		(27)	1236
C$_{25}$				
	Bu$_3$SnH, AIBN, toluene, reflux		(72)^b	1237, 1238

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{25} 	Bu_3SnH, AIBN, toluene	 (33)	1239
C_{26} 	Bu_3SnH, AIBN, benzene, 80°	 **I** +  **II** R^1 | R^2 | **I** | **II** TBS | Piv | (67) | (30) —CMe_2— | | (60) | (—)	251, 252
 R = H, Me	Bu_3SnH, toluene, reflux	 (50)	107
	Bu_3SnH, AIBN, toluene	 (63)	269

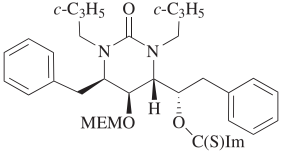
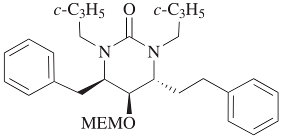
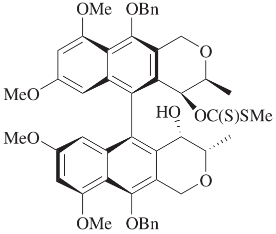
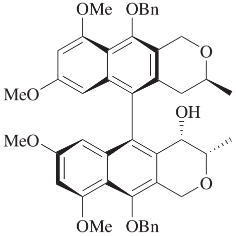
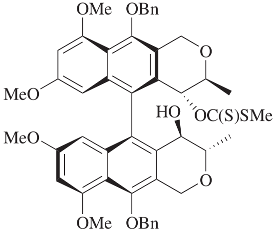
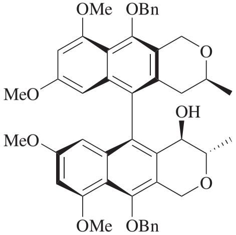
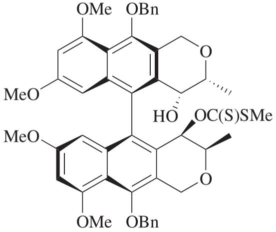
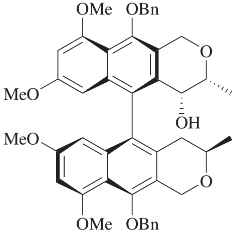
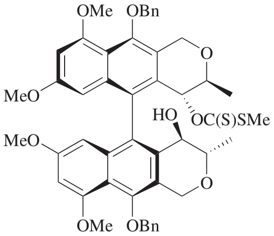
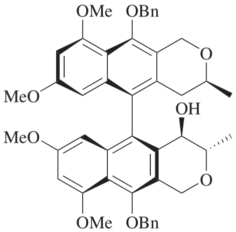
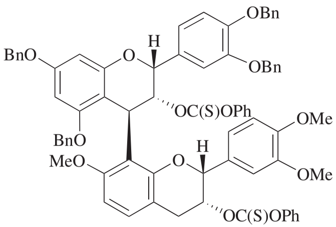
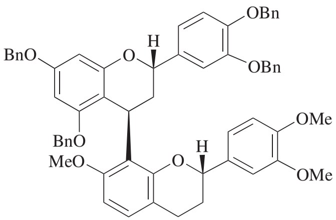
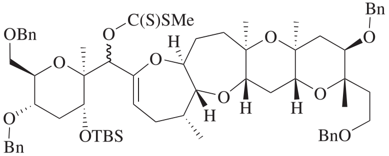
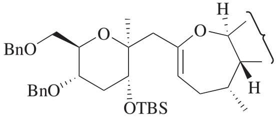
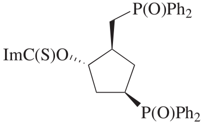
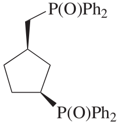
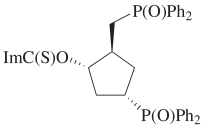
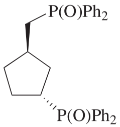
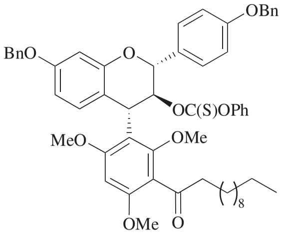
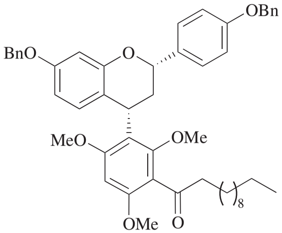
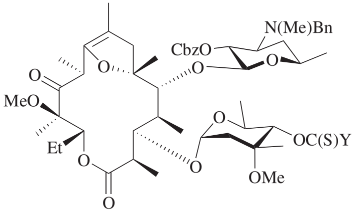
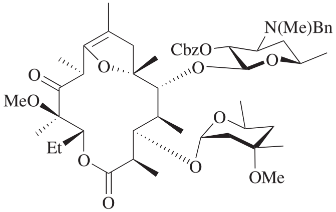
C_{27}				
	Bu_3SnH, AIBN, toluene, reflux, 1 h		(—)	1240
C_{28}				
	Bu_3SnH, AIBN, toluene, 80°, 1 h		(89)	1241
	Bu_3SnH, AIBN, toluene, 80°, 1 h		(—)	1241
	Bu_3SnH, AIBN, toluene, 80°, 1 h		(—)	1241

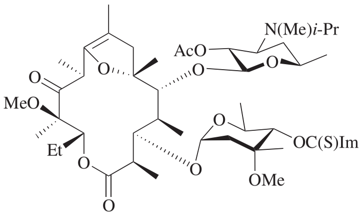
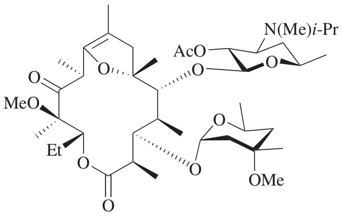
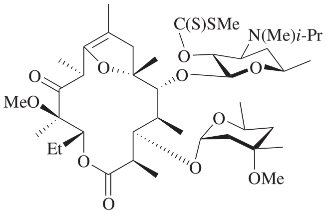
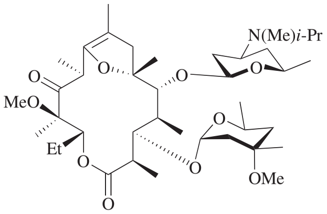
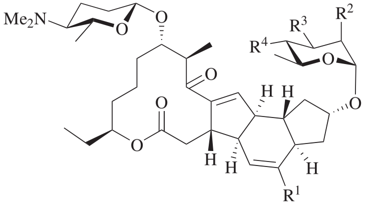
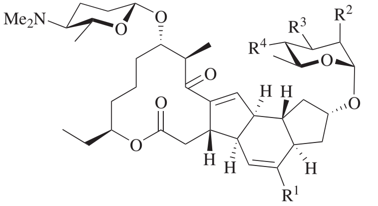
TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}			
	Bu_3SnH, AIBN, toluene, 80°, 1 h	 (—)	1241
C_{30}			
	H_3PO_2, Et_3N, AIBN, dioxane, reflux, 1.25 h	 (70)	1242
	Bu_3SnH, AIBN, benzene, 80°	 (75)	252
	Bu_3SnH, AIBN, toluene, reflux, 4–6 h	 (56)	1243

		Bu$_3$SnH, AIBN, toluene, reflux, 4–6 h	 (—)	1243
C_{33}		Bu$_3$SnH, AIBN, toluene, 100°		1244
C_{34}		MH, amine, AIBN, solvent, reflux		197

Y	MH	Amine	Solvent	Time (h)	
MeS	Bu$_3$SnH	—	toluene	1	(51)
MeS	H$_3$PO$_2$	Et$_3$N	dioxane	1	(72)
MeS	H$_3$PO$_2$	Et$_3$N	DME	4.5	(69)
MeS	H$_3$PO$_2$	Et$_3$N	MeCN	3	(69)
MeS	H$_3$PO$_2$	EtN(*i*-Pr)$_2$	dioxane	1	(68)
MeS	H$_3$PO$_2$	EtN(*i*-Pr)$_2$	toluene	3.5	(62)
Im	H$_3$PO$_2$	Et$_3$N	dioxane	3	(51)
Im	H$_3$PO$_2$	Et$_3$N	DME	8	(44)
Im	H$_3$PO$_2$	EtN(*i*-Pr)$_2$	dioxane	5	(35)
PhNH	H$_3$PO$_2$	Et$_3$N	dioxane	2.5	(trace)

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{34}			
	Ph_3SnH, AIBN, toluene, reflux	 (46)[b]	265
	Ph_3SnH, AIBN, toluene, reflux	 (50)	265
$C_{36–37}$			
	Bu_3SnH, AIBN, toluene, reflux, 8–20 h		1245

R^1	R^2	R^3	R^4
H	OC(S)SMe	OMe	OMe
H	OMe	OC(S)SMe	OMe
H	OMe	OMe	OC(S)SMe
Me	OMe	OC(S)SMe	OMe

R^1	R^2	R^3	R^4	
H	H	OMe	OMe	(84)
H	OMe	H	OMe	(76)
H	OMe	OMe	H	(37)
Me	OMe	H	OMe	(74)

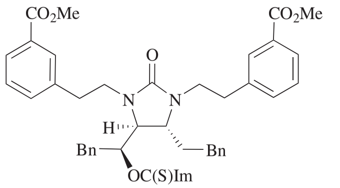
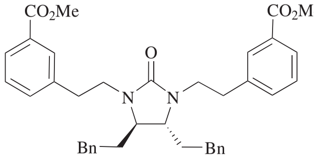
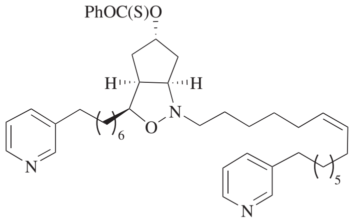
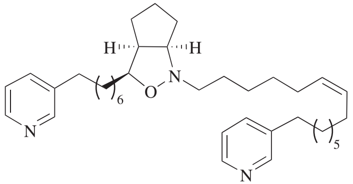
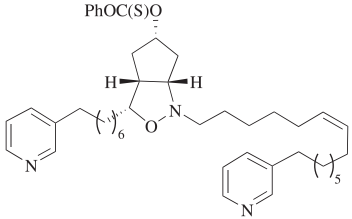
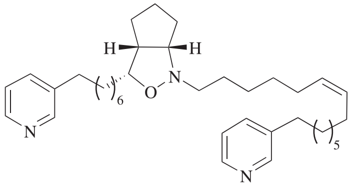
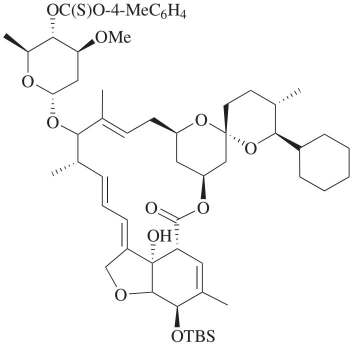
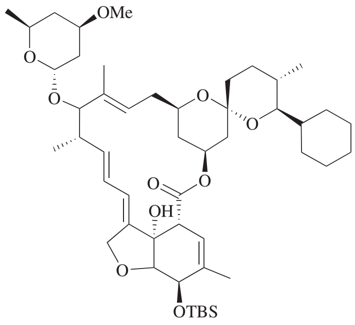
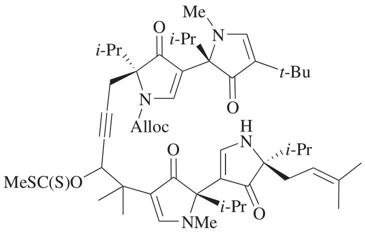
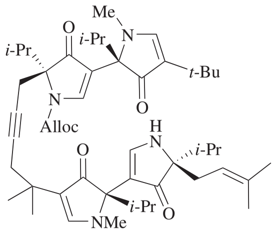
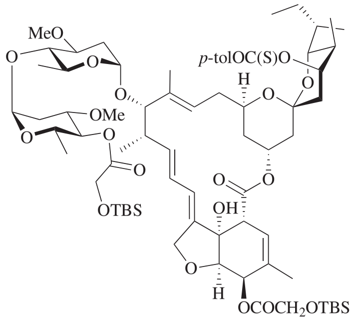
C_{37}		Bu_3SnH, AIBN, toluene, reflux, 1 h		(—)	1240
C_{38}		$(TMS)_3SiH$, AIBN		(69)	1246
		$(TMS)_3SiH$, AIBN		(65)	1246

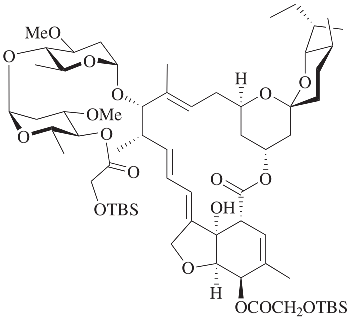
TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{42}$			
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (76)	267
C$_{44}$			
	Ph_3SnH, Et_3B, benzene, 10°, 10 min	 (85)[a]	1247

C_{46}



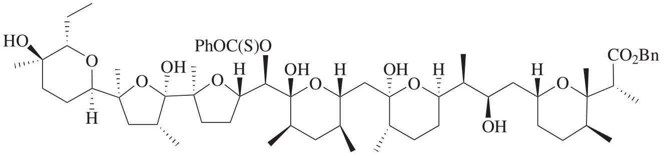
Bu_3SnH, AIBN, toluene, reflux, 1 h



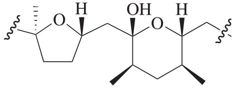
(72)

1248

C_{48}



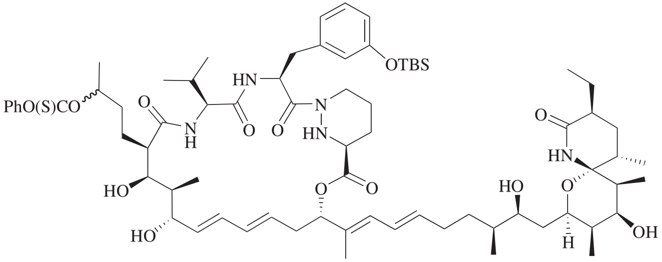
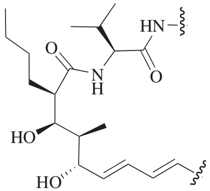
$(TMS)_3SiH$, AIBN, toluene, 80°, 1.5 h



(75)

1249

TABLE 2H. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{60}			
	Bu_3SnH, AIBN, benzene, reflux, 0.75 h	 (36)	1250

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[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 3. TERTIARY ALCOHOLS

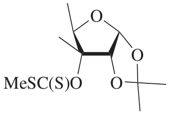
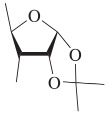
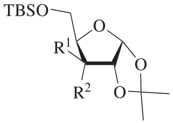
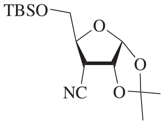
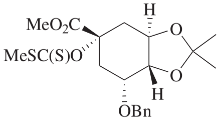
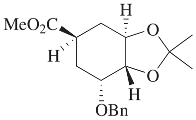
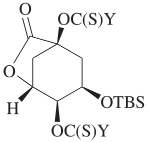
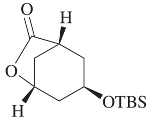
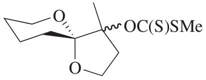
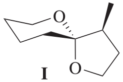
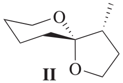
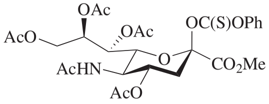
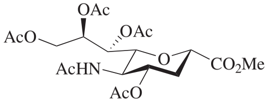
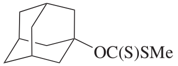
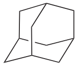
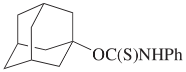
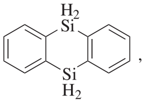
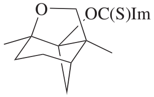
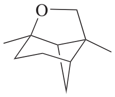
	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		Bu_3SnH, AIBN, toluene, reflux, 2.5 h	 (87)	40
		Bu_3SnH, AIBN, toluene, 70°, 4 h	 R^1 / R^2 PhOC(S)O / CN (76) CN / PhOC(S)O (60)[a]	1251, 692
C_7		Bu_3SnH, AIBN, toluene	 (75)	44
		Bu_3SnH, AIBN, toluene, reflux	 Y Im (55) SMe (71)	1252, 1253
C_9		Bu_3SnH, AIBN, toluene, reflux, 8 h	 **I** +  **II** **I** + **II** (90)	1254
		Bu_3SnH, AIBN, toluene, 100°, 5 h	 (—)	1255

TABLE 3. TERTIARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{10}$ 	$Ph_2SiHSiHPh_2$, AIBN, EtOAc, reflux, 16 h	 **I** (86)	186
	EPHP, ACVA, CTAB, H_2O, 80°, 5 h	**I** (14)	199
	H_3PO_2, NEP, dioxane, reflux, 1 h	**I** (100)	193
	$R_2P(O)H$, initiator, dioxane, reflux	**I** R Initiator Time (h) Bu ACCN 8 (90) Ph (t-Bu)$_2$O$_2$ 16 (85)	205 206
	$(MeO)_2P(O)H$, Et_3N, AIBN, dioxane, reflux, 1 h	**I** (100)	194
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), DMF, 75°, 0.5 h	**I** (100)	211
	$(TMS)_3SiH$, AIBN, benzene, reflux, 1 h	**I** (85)	39
	 , AIBN, benzene, reflux, 2 h	**I** (85)	76
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 (80)	79

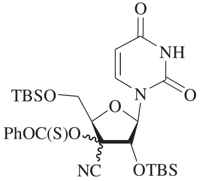
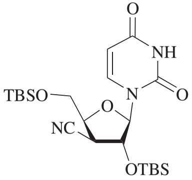
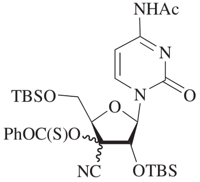
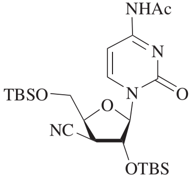
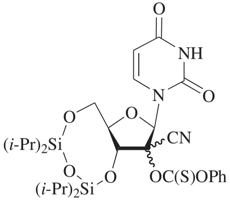
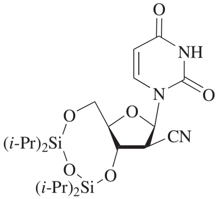
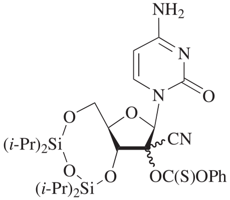
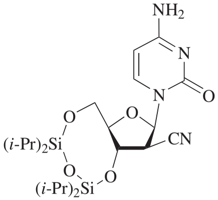
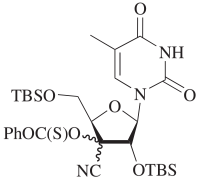
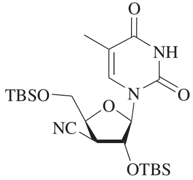
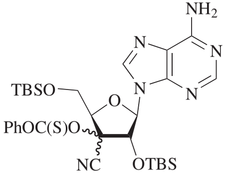
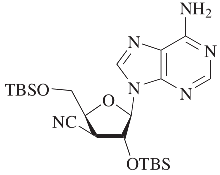
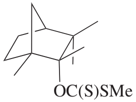
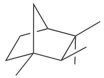
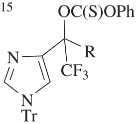
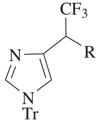
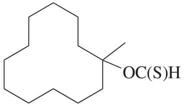
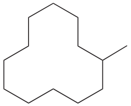
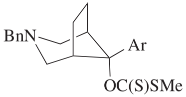
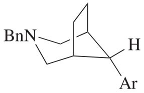
	Bu_3SnH, AIBN, toluene, 70°, 4 h		(68)	41
	Bu_3SnH, AIBN, toluene, 70°, 4 h		(65)[a]	41
	Bu_3SnH, AIBN, toluene, reflux		(40)[b]	1256
	Bu_3SnH, AIBN, toluene, reflux		(42)[b]	1256

TABLE 3. TERTIARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	Bu_3SnH, AIBN, toluene, 70°, 4 h	 (60)	692, 693
	Bu_3SnH, AIBN, toluene, 70°, 4 h	 (—)	41
	Bu_3SnH, Et_3B, O_2, rt	 (74)	81
C_{11-15}			
	Bu_3SnH, AIBN, benzene, 80°, 3 h	 R Ph (94) 1-naphthyl (66)	877
C_{13}			
	Bu_3SnH, benzene, reflux	 (71)	33
	Bu_3SnH, AIBN, benzene, reflux, 12 h	 Ar Ph (82) 4-ClC_6H_4 (76)	1257

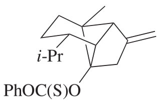
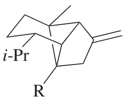
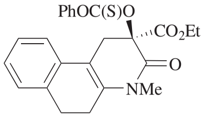
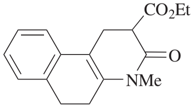
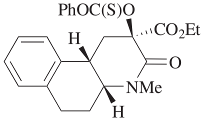
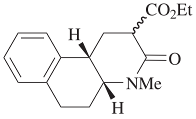
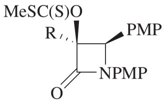
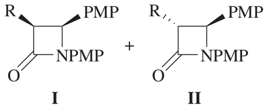
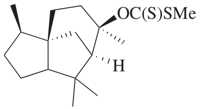
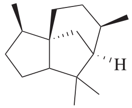
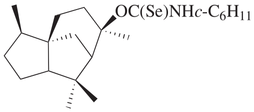
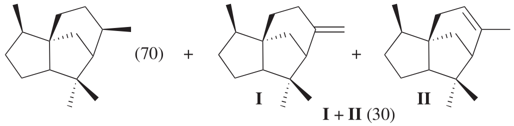
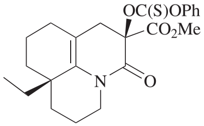
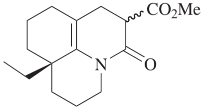
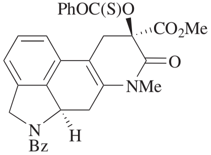
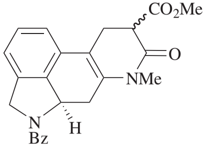
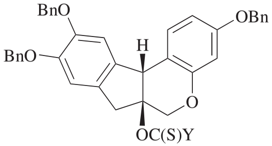
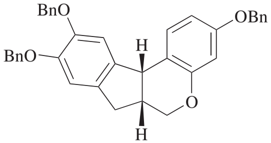
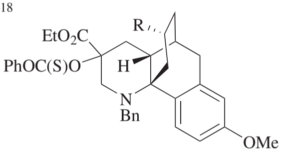
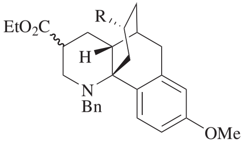
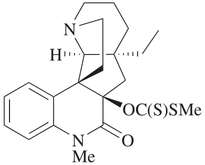
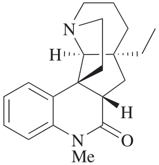
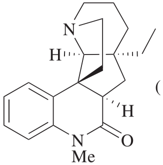
C_{14} 	Bu_3SnH, AIBN, cumene, reflux, 2.5 h	 R H (25) $HSCH_2O$ (14) $PhOCH_2O$ (15)	1258
	Bu_3SnH, AIBN, toluene, 75°, 1.5 h	 (83)	1259
	Bu_3SnH, AIBN, toluene, 75°, 1.5 h	 (98)	1259
C_{14-23} 	Bu_3SnH, AIBN, toluene, reflux, 3 h	 R — I + II — I:II n-C_5H_{11} (96) 90:10 Ph (93) 95:5 n-C_6H_{13} (92) 90:10 n-C_9H_{19} (90) 94:6 $Ph(CH_2)_3$ (95) 70:30 n-$C_{10}H_{21}$ (90) 88:12 n-$C_{14}H_{29}$ (92) 88:12	225
C_{15} 	Bu_3SnH, Et_3B, O_2, benzene, rt	 (99)	81
	Bu_3SnH, Et_3B, O_2, benzene, rt	 (70) + I + II I + II (30)	78

TABLE 3. TERTIARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	Bu_3SnH, AIBN, toluene, 75°, 8 h	 (70)	80
	Bu_3SnH, AIBN, toluene, 90°, 8 h	 (19)	1259
C_{16} 	Bu_3SnH, AIBN, benzene, reflux, 0.5 h	 Y OPh (71) OC_6F_5 (84)	1260
C_{17-18} 	Bu_3SnH, AIBN, toluene, 45–75°, 5 h	 R H (80) Me (96)	248
C_{19} 	Bu_3SnH, AIBN, toluene, reflux, 1.5 h	 (72) +  (15)	1261

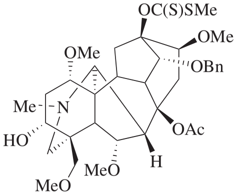
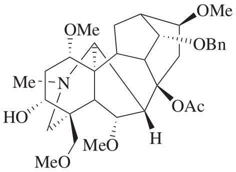
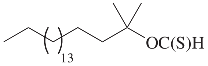
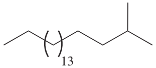
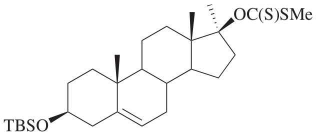
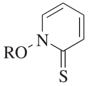
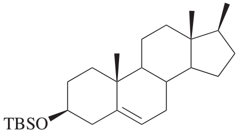
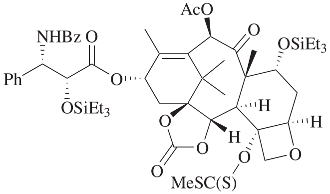
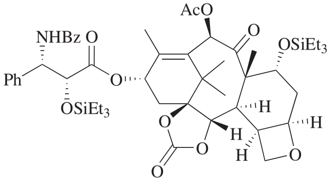
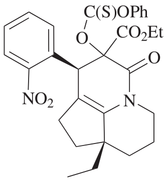
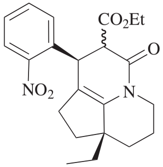
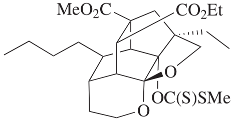
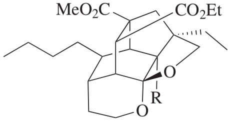
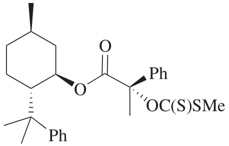
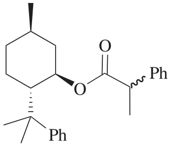
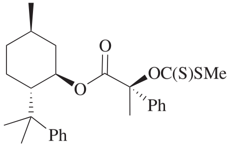
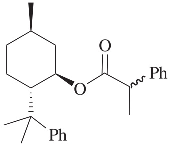
	Bu_3SnH, AIBN, toluene, reflux	 (83)	1214
C_{20} 	Bu_3SnH, benzene, reflux	 (83)	33
	 , MH, *hν*, 0°	 **I** R / MH *c*-C_5H_9 / Bu_3SnH (83) *c*-C_5H_9 / Ph_3SiH (75) Bz / Bu_3SnH (75)	81
	Bu_3SnH, Et_3B, O_2, rt	**I** (91)	81
	Bu_3SnH, TrN=NPh, 40°	**I** (99)	81
	$(EtO)_2POH$, Et_3B, O_2, rt	**I** (87)	81
	Bu_3SnH, AIBN, toluene, 90°	 (80)	1262

TABLE 3. TERTIARY ALCOHOLS (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	Bu_3SnH, AIBN, toluene, 75°, 12 h	 (88)	80
C_{21}			
	Me_3B (2.5–4.0 eq), R_2O (x eq), O_2 (0.8 eq as air, added slowly), benzene, rt	 R x H 5 (99) D 20 (90)	38
C_{25}			
	Bu_3SnH, AIBN, benzene, reflux	 (—) (R)/(S) = 7:3	1263
	Bu_3SnH, AIBN, benzene, reflux	 (—) (R)/(S) = 7:3	1263

[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 4. CYCLIC THIOCARBONATES

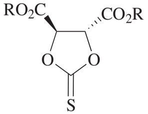
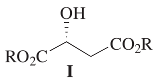
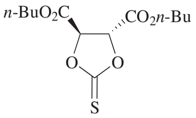
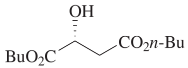
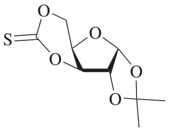
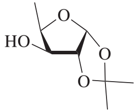
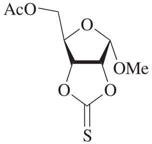
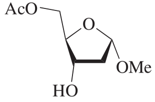
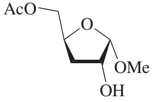
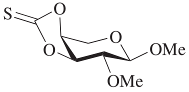
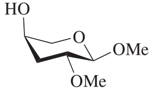
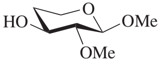
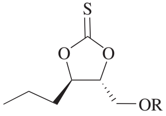
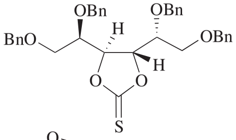
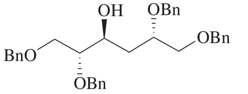
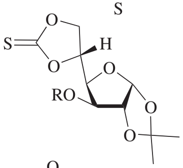
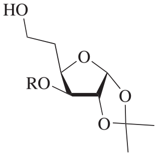
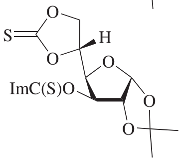
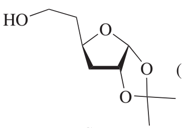
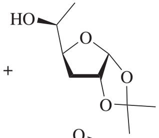
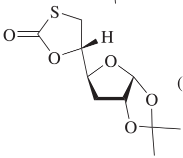
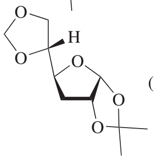
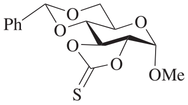
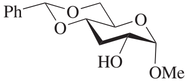
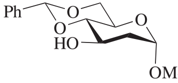
Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	Bu_3SnH, toluene, reflux, 20 min	 **I** R / Solvent / Time (min) Me / toluene / 20 / (88) *t*-Bu / benzene / 60 / (25)	1264, 1265
	$PhSiH_3$ (2 eq) or Ph_2SiH_2 (2 eq), AIBN (0.5 eq, added slowly), benzene, reflux, 1–2 h	**I** R / **I** Me / (92–93) Et / (90) Bu / (93–95)	226
	H_3PO_2 (*x* eq), AIBN (0.2 eq), Et_3N (*y* eq), dioxane, 80°	 *x* / *y* / Time (h) 5.0 / 5 / 0.5 / (35) 5.0 / 0 / 0.5 / (91) 3.5 / 0 / 0.5 / (92) 2.5 / 0 / 1.5 / (84) 1.5 / 0 / 2.0 / (83)	227
C_5 	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), Et_3N (8 eq), DMF, 65°, 0.25 h	 (75)	211
	Bu_3SnH, AIBN, toluene, reflux, 6.5 h	 (55)[a] +  (25)[a]	85
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (31) +  (23)	266

TABLE 4. CYCLIC THIOCARBONATES (*Continued*)

Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	MH, AIBN, solvent, reflux	 R | MH | Solvent | Time (h) | **I + II** | **I:II** Me | Bu_3SnH | toluene | 4 | (—) | 1.5:1 Bn | $(TMS)_3SiH$ | benzene | 5 | (59) | 1:1.7	30
	Bu_3SnH, AIBN	 (66)	1267
	Bu_3SnH, AIBN, reflux	 R | Solvent | Time (h) | H | dioxane | 2 | (71) Me | toluene | 6 | (59)	231 85
	Bu_3SnH, toluene, reflux	 (41) +  (18) +  (9) +  (14)	456
	nBu$_3$SnH, AIBN, toluene, reflux, 7 h	 (60) +  (30)	85

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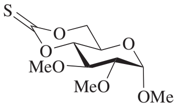
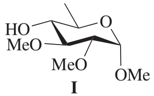
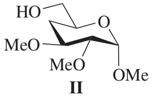
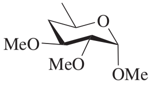
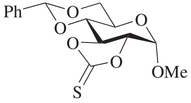
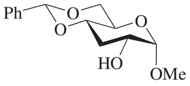
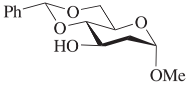
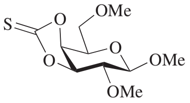
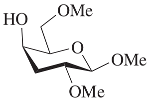
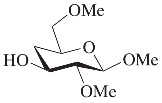
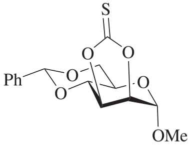
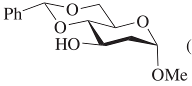
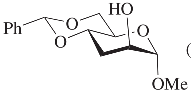
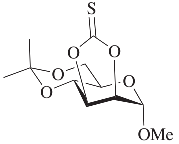
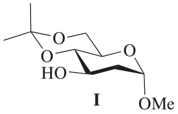
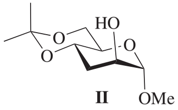
<tr><td></td><td>[MH (1.5 eq) + initiator]
(added slowly),
toluene, reflux</td><td> I +  II
<table>
<tr><th>MH</th><th>Initiator</th><th><i>x</i></th><th>I + II</th><th>I:II</th></tr>
<tr><td>Bu_3SnH</td><td>AIBN</td><td>(—)</td><td>(—)</td><td>91:9</td></tr>
<tr><td>$(TMS)_3SiH$</td><td>AIBN</td><td>(—)</td><td>(—)</td><td>92:8</td></tr>
<tr><td>Ph_3SiH</td><td>1,1-(t-$BuO_2)_2c$-C_6H_{10}</td><td>1.3</td><td>(—)</td><td>88:12</td></tr>
</table></td><td>36</td></tr>
<tr><td></td><td>Ph_3SiH (3 eq), toluene, reflux</td><td> (—)</td><td>36</td></tr>
<tr><td></td><td>Bu_3SnH, AIBN,
toluene, reflux, 7 h</td><td> (60) +  (30)</td><td>85</td></tr>
<tr><td></td><td>Bu_3SnH, AIBN,
toluene, reflux, 3 h</td><td> (31) +  (23)</td><td>1266</td></tr>
<tr><td></td><td>Bu_3SnH, AIBN,
toluene, reflux, 3 h</td><td> (54) +  (34)</td><td>1266</td></tr>
<tr><td></td><td>Bu_3SnH, AIBN,
toluene, reflux, 3 h</td><td> I +  II
I + II (79), I:II = 3:2</td><td>1266</td></tr>
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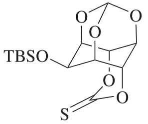
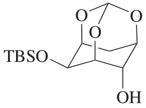
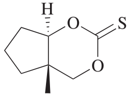
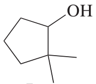
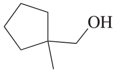
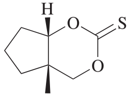
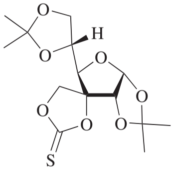
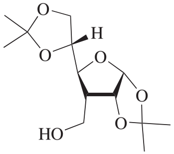
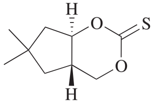
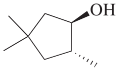
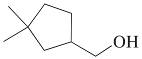
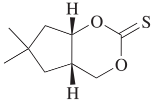
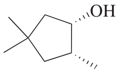
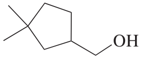
TABLE 4. CYCLIC THIOCARBONATES (*Continued*)

Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Bu_3SnH, AIBN, toluene, reflux, 100 min	 (65)	1268
C_7 	Bu_3SnH	 **I** +  **II** **I** + **II** (50), **I**:**II** = 47:1	84
	Bu_3SnH	**I** + **II** (61), **I**:**II** = 1:32	84
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (53)	232
C_8 	Bu_3SnH	 **I** +  **II** **I** + **II** (55), **I**:**II** = 21:1	84
	Bu_3SnH	 **I** +  **II** **I** + **II** (55), **I**:**II** = 1:19	84

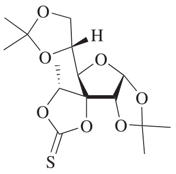
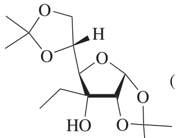
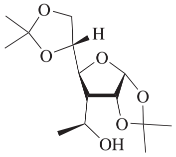
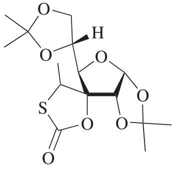
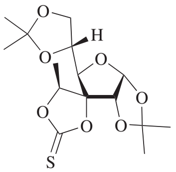
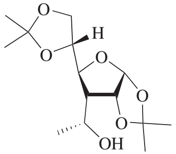
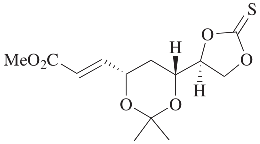
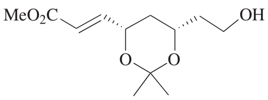
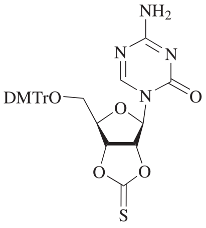
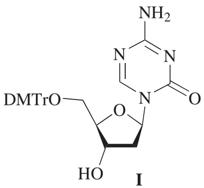
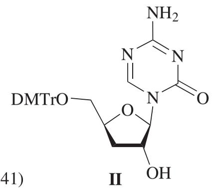
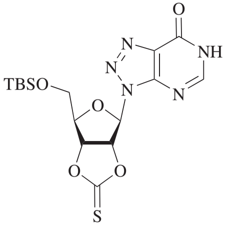
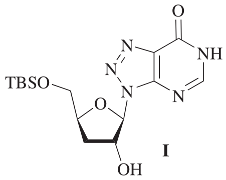
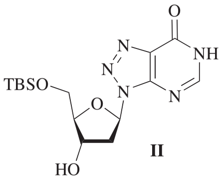
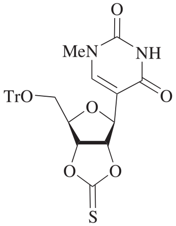
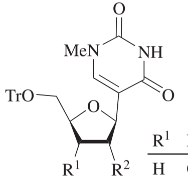
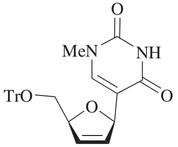
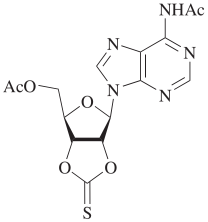
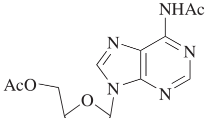
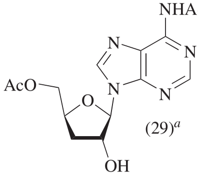
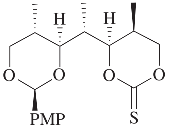
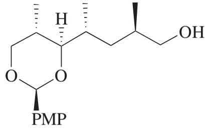
	Bu$_3$SnH, AIBN, toluene, reflux, 2 h	 **I** (33) +  (30) +  (21)	232
	Bu$_3$SnH, AIBN, toluene, reflux, 2 h	**I** (40) +  (40)	232
	Bu$_3$SnH, AIBN, benzene, reflux	 (—)	460
C$_8$			
	Bu$_3$SnH, AIBN, toluene, reflux, 2 h	 **I** +  **II** **I + II** (41)	607

TABLE 4. CYCLIC THIOCARBONATES (*Continued*)

Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 **I** +  **II** **I** + **II** (75), **I**:**II** = 1:1	234
	Bu_3SnH, AIBN, toluene, reflux, 5 h	 R^1 R^2 H OH (25) OH H (45) +  (18)	233
C_{10}			
	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (60)[a] +  (29)[a]	85
	Bu_3SnH, AIBN, toluene, reflux	 (75)	1269

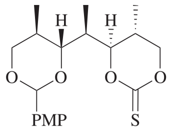
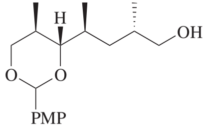
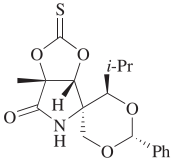
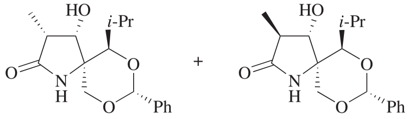
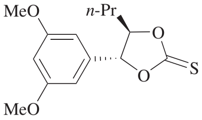
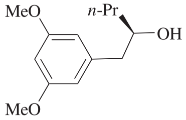
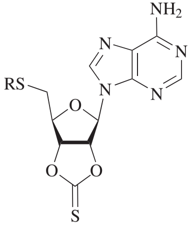
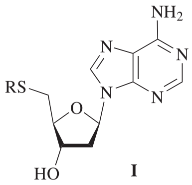
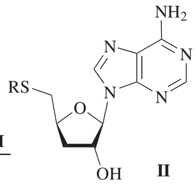
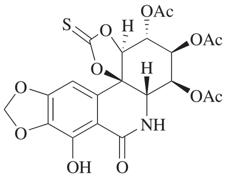
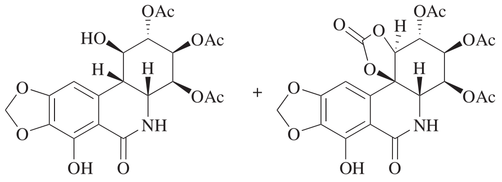
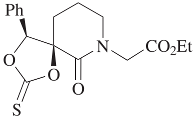
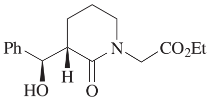
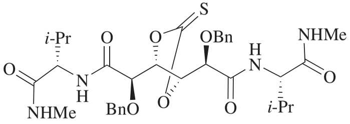
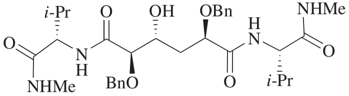
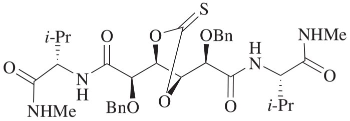
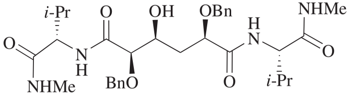
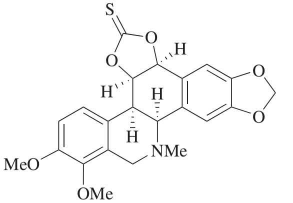
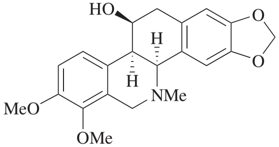
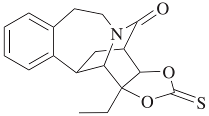
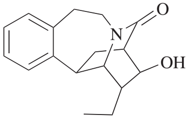
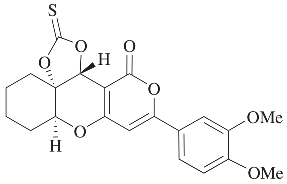
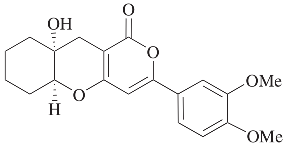
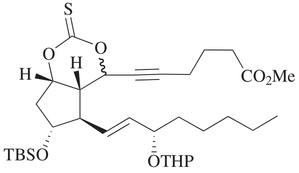
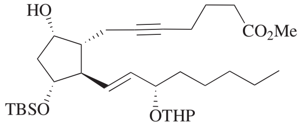
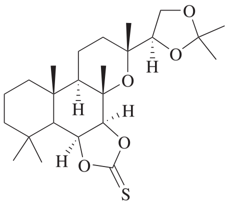
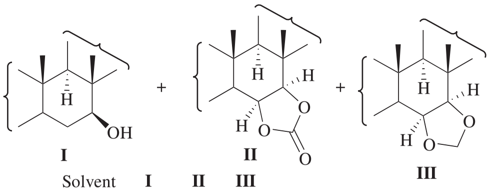
	Bu_3SnH, AIBN, toluene, reflux	 (84)	1270
	Bu_3SnH, AIBN, toluene, reflux	 **I** **I + II** (94), **I**:**II** = 1:3.6 **II**	1271
C_{11}			
	Bu_3SnH, AIBN, benzene, reflux, 1.5 h	 (94)	228
	Bu_3SnH, AIBN, toluene, reflux	 **I** +  **II** R | **I + II** CHF_2 (45) CF_3 (45)	1272
C_{13}			
	Bu_3SnH, AIBN, toluene, reflux	 (50) (22)	1273

TABLE 4. CYCLIC THIOCARBONATES (*Continued*)

Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	$(TMS)_3SiH$, AIBN, toluene, 100°	 (47)	1274
C_{16} 	Bu_3SnH, AIBN, toluene, reflux	 (33)	1275
	Bu_3SnH, AIBN, toluene, reflux	 (34)	1275
C_{17} 	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (54)	1276
	Bu_3SnH, Bz_2O_2, toluene, reflux,	 (65)	1277

C_{18} 	Bu_3SnH (neat), AIBN, sealed tube, 130°		(73)	230
C_{20} 	Bu_3SnH, $(t\text{-}Bu)_2O_2$, 50°, 50 min		(77)[a]	229
	Bu_3SnH, AIBN, solvent, reflux	 **I** + **II** + **III**		237

Solvent	**I**	**II**	**III**
dioxane	(90)	(2)	(6)
toluene	(52)	(18)	(18)

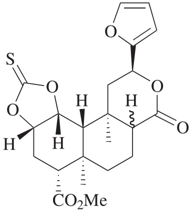
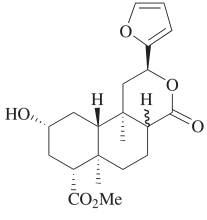
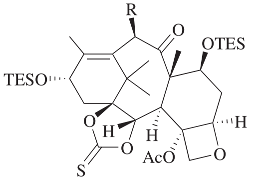
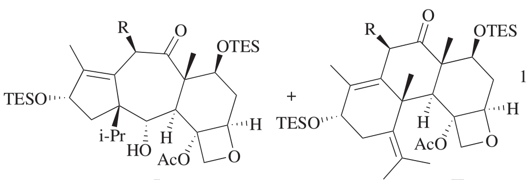
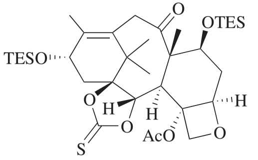
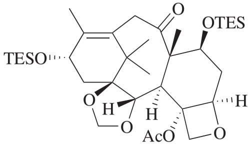
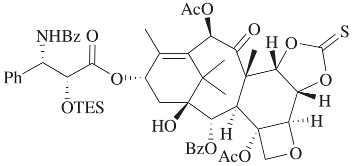
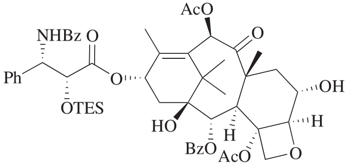
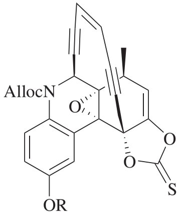
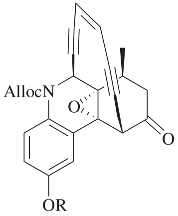
	Bu_3SnH, AIBN, toluene, 80°		(47)	1278

TABLE 4. CYCLIC THIOCARBONATES (*Continued*)

	Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}		Bu_3SnH, AIBN, toluene, 90–100°, 3 h	 **I** **II** R I II H (42)[a] (21)[a] AcO (21)[a] (0)	143
		Ph_3SnH, AIBN, toluene, 100°, 3 h	 (81)	143
		Bu_3GeH, AIBN, THF–toluene, 100°	 (71)	1279
		Bu_3SnH, AIBN, toluene, 70°	 R Me (60) TBS (97)	247 247, 248

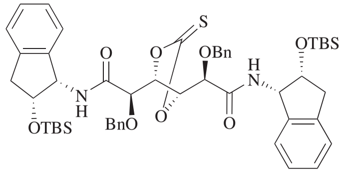
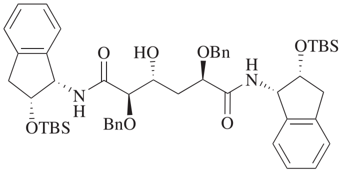
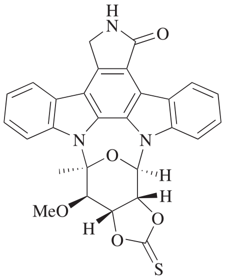
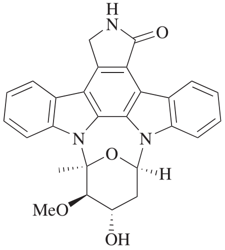
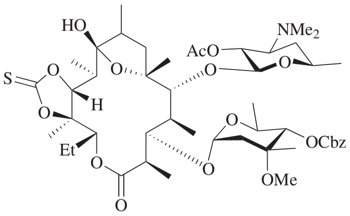
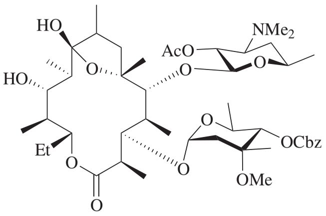
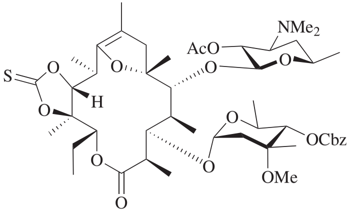
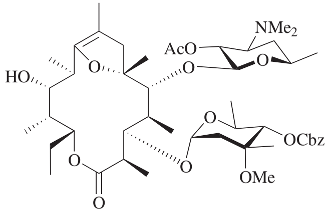
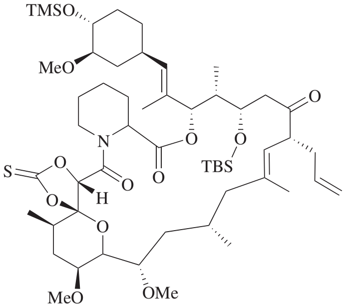
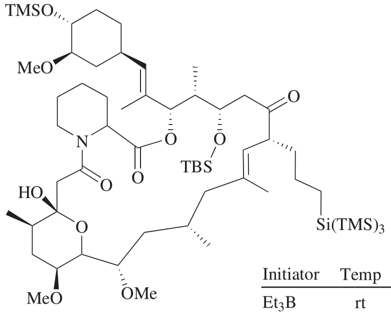
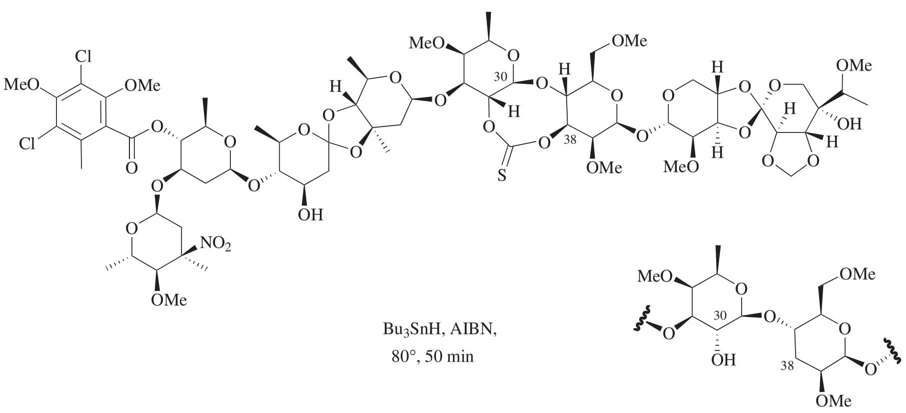
C_{24} 	Bu$_3$SnH, AIBN, toluene, reflux		(20)	1275
C_{26} 	Bu$_3$SnH, AIBN, toluene		(47)	269
C_{34} 	Bu$_3$SnH, AIBN, toluene		(—)	1280

TABLE 4. CYCLIC THIOCARBONATES (*Continued*)

Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{34}			
	Bu_3SnH, AIBN, toluene	 (—)	1280
C_{41}			
	$(TMS)_3SiH$, initiator, benzene	 Initiator / Temp Et_3B / rt / (38) AIBN / reflux / (54)	182

C_{58}



Bu_3SnH, AIBN,
80°, 50 min

(15) 1281

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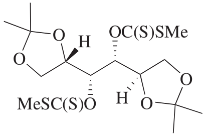
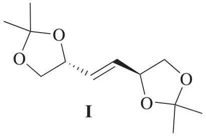
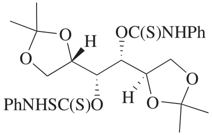
[a] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 5. 1,2-BIS(XANTHATES) AND RELATED SUBSTRATES

Bis(xanthate) or Related Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Bu_3SnH, AIBN, toluene, reflux	 **I** (65)	239
	Ph_2SiH_2 (2.2 eq), AIBN (x eq), toluene, reflux	**I** x Time (h) 1.2 6 $(92)^a$ 1.8 4.5 $(100)^a$	244
	Et_3SiH (neat), Bz_2O_2 (0.8 eq, added in portions), reflux, 2 h	**I** (82)	171, 367
	H_3PO_2, AIBN, Et_3N, dioxane, reflux	**I** $(25)^a$	194
	H_3PO_2 (5 eq), Et_3N (5.5 eq), olefin (x eq), dioxane, reflux, 1 h	**I** Olefin x n-$C_{10}H_{21}CH{=}CH_2$ 1.5 $(78)^a$ n-$C_{10}H_{21}CH{=}CH_2$ 5 $(60)^a$ n-$BuOCH{=}CH_2$ 5 $(62)^a$	194
	EPHP (10 eq), initiator (x eq), CTAB (2 eq), solvent	**I** Initiator x Solvent Temp Time (h) ACVA 0.75 H_2O 80° 9 (85) Et_3B 5 EtOH rt 5 (79)	199
	$(Bu_4N)_2S_2O_8$ (3 eq), HCO_2Na (6 eq), Na_2CO_3 (8 eq), 65°, 60 min	**I** (86)	211
	MH (2 eq), initiator (0.2 eq), solvent	**I** MH Initiator Solvent Temp (°) Time (h) Ph_3SiH $(t\text{-}Bu)_2O_2$ PhCl 130 4 (46) Ph_2SiH_2 $(t\text{-}Bu)_2O_2$ PhCl 130 4 (62) $(TMS)_3SiH$ AIBN benzene 80 3 (84) Bu_3SnH AIBN benzene 80 4 (43)	88

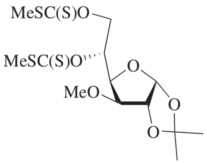
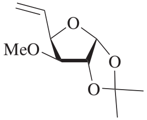
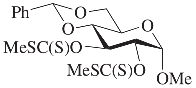
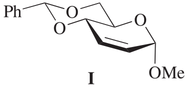
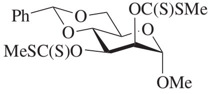
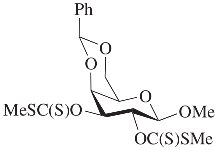
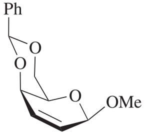
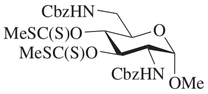
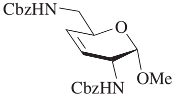
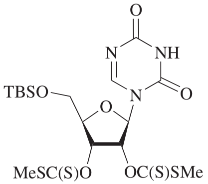
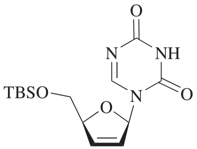
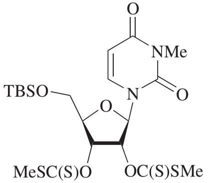
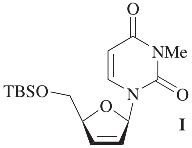
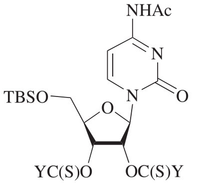
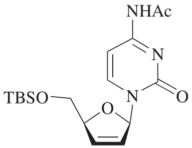
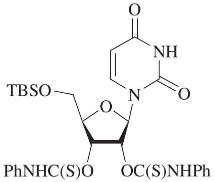
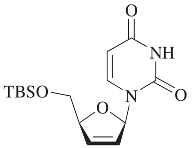
C$_6$ 	MH, initiator, toluene, reflux	 MH Initiator Bu_3SnH none (62) Ph_2SiH_2 AIBN (88)	239 244
	Bu_3SnH, AIBN, toluene, reflux	 **I** (59)	239
	Polystyrene-linked-Bu_2SnH, AIBN, toluene, 80°, 9 h	**I** (98)	104
	Ph_2SiH_2, AIBN, toluene, reflux, 1 h	**I** (97)	244
	EPHP (10 eq), ACVA (0.75 eq), CTAB (2 eq), H_2O, 80°, 8 h	**I** (83)	199
	n-$C_{16}H_{33}NMe_3^+ H_2PO_2^-$ (3 eq), ACVA (0.5 eq), H_2O, reflux, 7 h	**I** (80)	201
	Bu_3SnH, AIBN, toluene, reflux	**I** (79)	239
	Bu_3SnH, AIBN, toluene, reflux	 (49)	239
	Bu_3SnH, toluene, reflux, 2 h	 (80)	61

TABLE 5. 1,2-BIS(XANTHATES) AND RELATED SUBSTRATES (*Continued*)

Bis(xanthate) or Related Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	EPHP (10 eq), ACVA (0.75 eq), CTAB (2 eq), H_2O, 80°, 9 h	 (95)	199
C_9 	Ph_2SiH_2, AIBN, toluene, reflux, 80 min	 **I** (91)	244
	n-$C_{16}H_{33}NMe_3^+ H_2PO_2^-$ (3 eq), ACVA (0.5 eq), H_2O, reflux, 7 h	**I** (82)	201
	MH, AIBN, solvent, reflux		
		MH | Y | Solvent | Time (h)	
		Bu_3SnH | MeS | toluene | 1 | (59)	86
		$(TMS)_3SiH$ | PhNH | benzene | 4 | (49)	88
	$(TMS)_3SiH$, AIBN, benzene, reflux, 4 h	 (69)	88

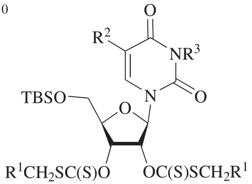
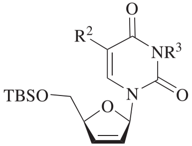
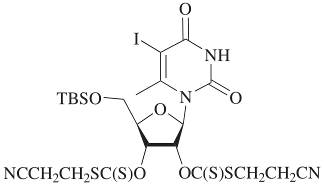
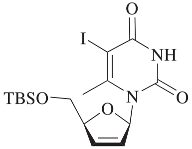
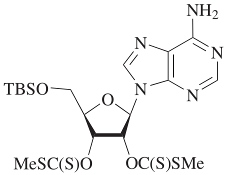
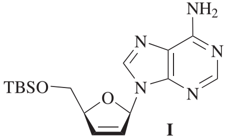
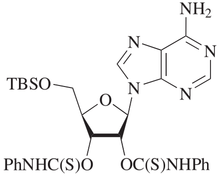
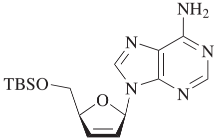
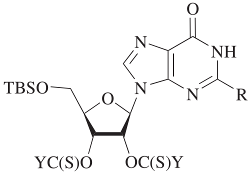
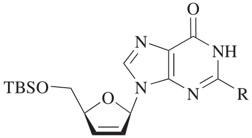
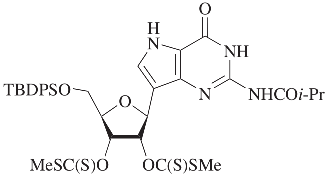
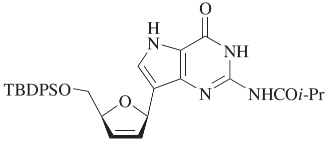
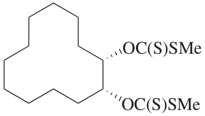
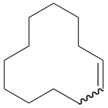
C_{9-10}		Bu_3SnH, AIBN, toluene, reflux, 1 h	 R^1 R^2 R^3 H H Me (64) CH_2CN H Me (87) CH_2CN Me H (65)	86
C_{10}		Bu_3SnH, AIBN, toluene, 90°	 (70)	87
		Bu_3SnH, AIBN, toluene, reflux, 1 h	 **I** (59)	86
		Ph_2SiH_2, AIBN, toluene, reflux, 1.3 h	**I** (95)	244
		Et_3SiH (neat), Bz_2O_2 (0.6 eq, added in portions), reflux, 1.5 h	**I** (100)	367
		$PhSiH_3$, AIBN, toluene, reflux, 80 min	**I** (95)	367
		n-$C_{16}H_{33}NMe_3^+$ $H_2PO_2^-$ (3 eq), ACVA (0.5 eq), H_2O, reflux, 7 h	**I** (76)	201
		EPHP (10 eq), initiator (x eq), CTAB (2 eq), solvent	**I** Initiator x Solvent Temp Time (h) ACVA 1.25 H_2O 80° 15 (58) Et_3B 5 EtOH rt 2 (76)	199

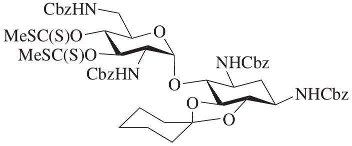
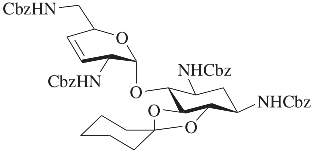
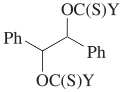
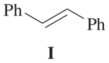
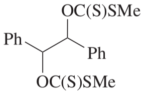
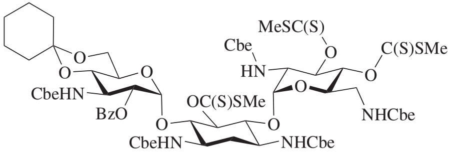
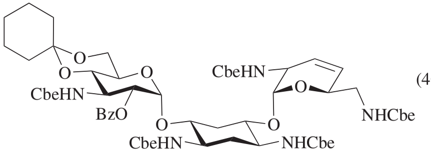
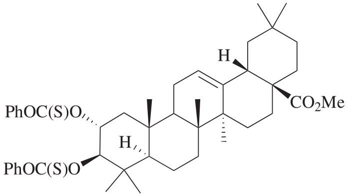
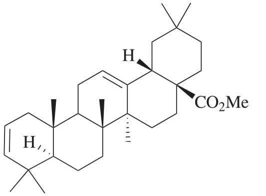
TABLE 5. 1,2-BIS(XANTHATES) AND RELATED SUBSTRATES (*Continued*)

Bis(xanthate) or Related Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	$(TMS)_3SiH$, benzene, reflux, 4 h	 (66)	88
	MH, AIBN, solvent, reflux		

Y	R	MH	Solvent	Time (h)		
MeS	NHCO*i*-Pr	$(TMS)_3SiH$	benzene	4	(93)	86
PhNH	NHCO*i*-Pr	Bu_3SnH	toluene	1	(57)	88
PhNH	H	$(TMS)_3SiH$	toluene	4	(71)	88

Bis(xanthate) or Related Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	Bu_3SnH, AIBN, toluene, 70°, 2 h	 (75)	395
C_{12}			
	EPHP (10 eq), initiator (x eq), CTAB (2 eq), solvent		199

Initiator	*x*	Solvent	Temp	Time (h)	
ACVA	0.75	H_2O	80°	8 h	(92)
Et_3B	0.5	EtOH	rt	1.5 h	(71)

C_{12}		Bu_3SnH, AIBN, toluene, reflux, 2 h		(64)	1282
C_{14}		Polystyrene-linked Bu_2SnH, AIBN, toluene, 80°	 **I** Y SMe (82) OPh (71)		104
		Ph_2SiH_2, AIBN, toluene reflux	**I** (63)		244
C_{18}		Bu_3SnH, toluene, reflux, 5 h		(40)	61
C_{30}		PMHS, $(Bu_3Sn)_2O$ (cat.), AIBN, toluene, 80°, 24 h		(70)	242

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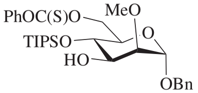
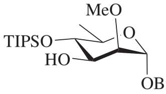
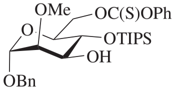
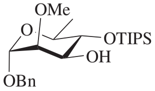
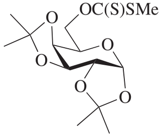
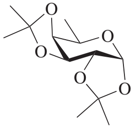
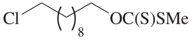
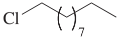
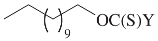
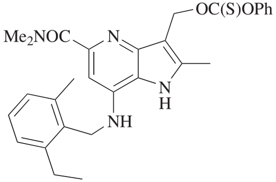
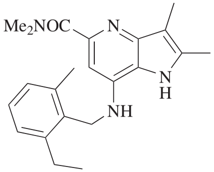
[a] The yield was determined by NMR.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009

A. PRIMARY ALCOHOLS

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		Bu_3SnH, AIBN, toluene, reflux	 (47)[a]	1283
		Bu_3SnH, AIBN, toluene, reflux	 (—)	1283
		$(TMS)_3SiH$ (1.2 eq), AIBN (0.1 eq), toluene, 130°, 5 min (flow microreactor)	 (93)	181
C_{10}		$(TMS)_3SiH$ (1.2 eq), AIBN (0.1 eq), toluene, 130°, 5 min (flow microreactor)	 (70)	181
C_{12}		$(TMS)_3SiH$ (1.2 eq), AIBN (0.1 eq), toluene, 130°, 5 min (flow microreactor)	 Y SMe (89) Im (94)	181
C_{20}		H_3PO_2, AIBN, Et_3N, dioxane, H_2O, 100°, 1 h	 (15)[b]	1284

[a] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

[b] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

B. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

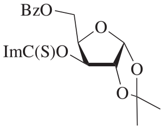
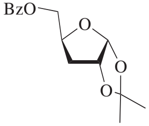
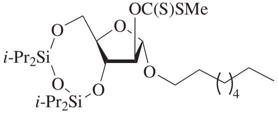
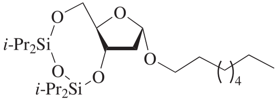
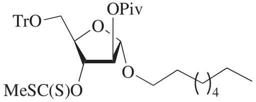
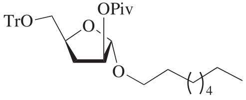
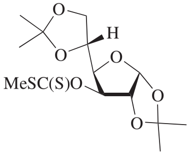
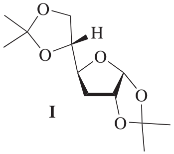
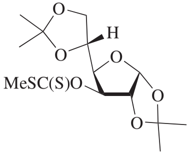
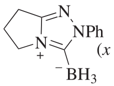
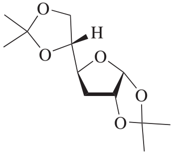
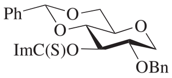
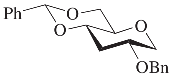
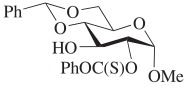
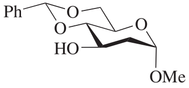
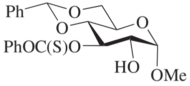
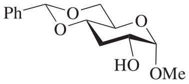
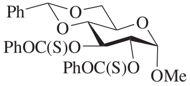
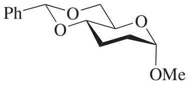
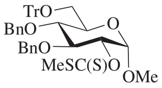
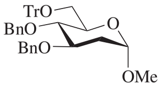
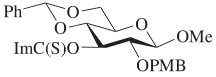
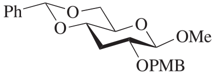
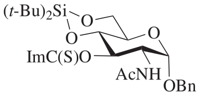
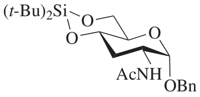
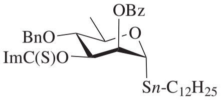
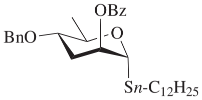
	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		$(MeO)_2P(O)H$, Bz_2O_2, dioxane, reflux, 2 h	 (92)	1285
		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (86)[a]	1286
		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (83)[a]	1286
C_6		Bu_3SnH, toluene, reflux, o/n	 **I** (84)	1287
		$(TMS)_3SiH$ (1.2 eq), AIBN (0.1 eq), toluene, 130°, 5 min (flow microreactor)	**I** (92)	181
		 (x eq), initiator (y eq), benzene, 2 h	 x Initiator y Temp 2 AIBN 0.5 — reflux (61) 1 Et_3B 1 O_2 rt (60)	213

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

B. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_6$ 	Bu_3SnH, AIBN, toluene, reflux, o/n	 (88)	1288
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (70)	67
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (72)	67
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (66)	67
	Bu_3SnH, AIBN, toluene, reflux	 (86)	1289
	Bu_3SnH, AIBN, toluene, reflux	 (78)	1290
	Bu_3SnH, AIBN, toluene, reflux	 (93)	1291
	Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (82)	1292

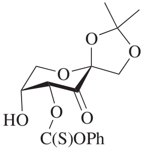
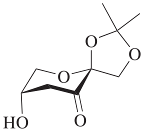
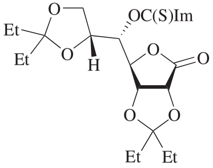
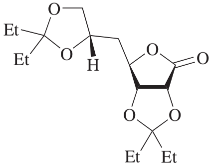
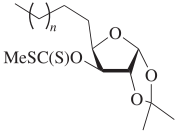
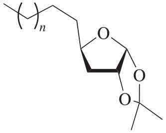
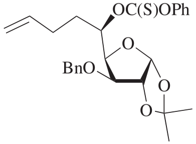
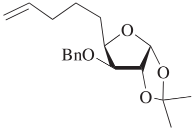
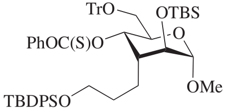
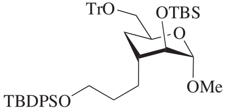
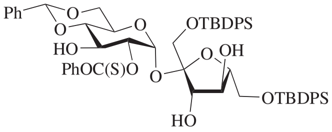
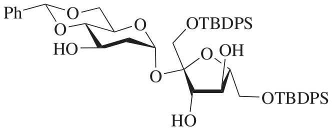
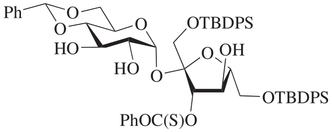
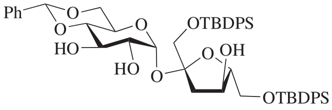
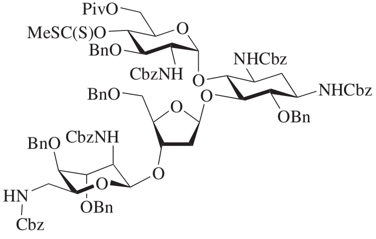
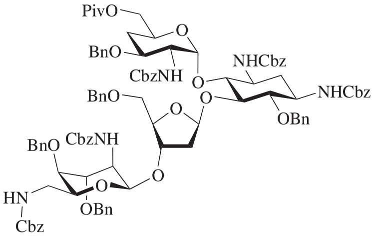
	Bu_3SnH, $(t\text{-}Bu)_2O_2$, toluene, reflux		(35)	1293
C_7				
	$(TMS)_3SiH$, AIBN, toluene, reflux, 1 h		(94)[a]	1294
$C_{8–10}$				
	$(TMS)_3SiH$, AIBN, benzene, reflux, 2 h		*n* 1 (85)[a] 3 (85)[a]	1295
C_9				
	Bu_3SnH, AIBN, toluene, reflux		(75)	1296
	Bu_3SnH, AIBN, toluene, reflux		(93)[b]	1297

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

B. SECONDARY ALCOHOLS: CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (48)	67
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (42)	67
C_{23}			
	H_3PO_2, Et_3N, AIBN, dioxane, reflux, 24 h	 (90)	1298

[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

C. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES

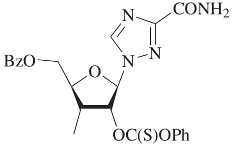
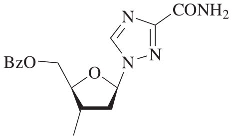
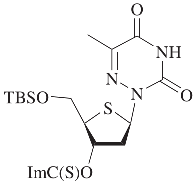
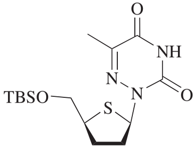
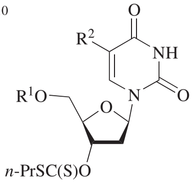
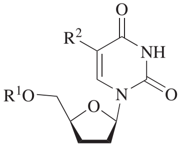
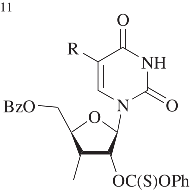
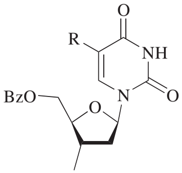
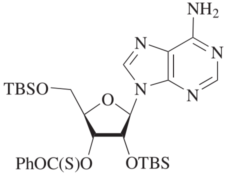
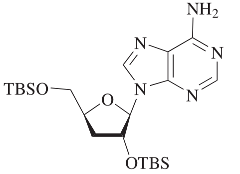
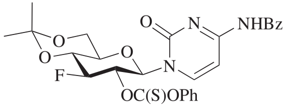
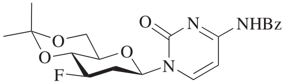
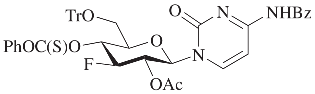
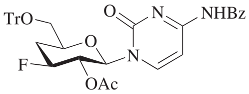
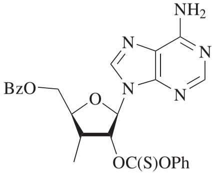
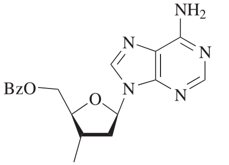
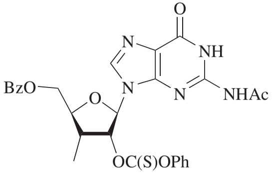
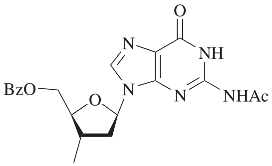
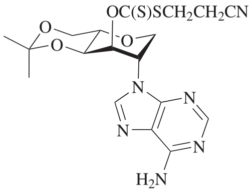
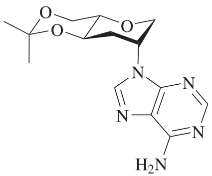
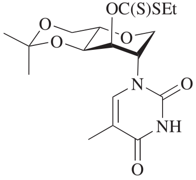
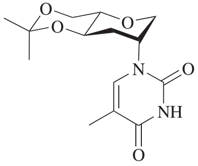
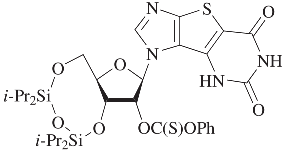
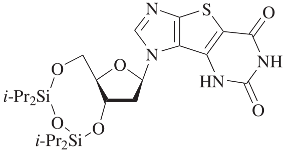
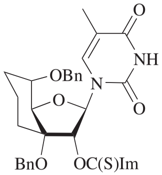
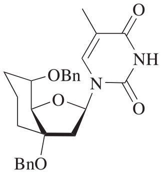
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	$(TMS)_3SiH$, AIBN, toluene, reflux, 4 h	 (59)[a]	1299
	Bu_3SnH, AIBN, toluene, 100°, 0.5 h	 (64)	1300
$C_{9–10}$			
	Bu_3SnH, AIBN, toluene, reflux, 1.25 h	 R^1 R^2 TBS H (61) Tr Me (68)	1301
$C_{10–11}$			
 R = H, Me	$(TMS)_3SiH$, AIBN, toluene, reflux, 3 h	 (90)[a]	1299

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

C. SECONDARY ALCOHOLS: NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (85)	1302
	Bu_3SnH, ACCN, toluene, 80°, 3 h	 (60)	1303
	Bu_3SnH, ACCN, toluene, 80°, 3 h	 (68)	1303
C_{11}			
	$(TMS)_3SiH$, AIBN, toluene, reflux, 3 h	 (56)[a]	1299
	$(TMS)_3SiH$, AIBN, toluene, reflux, 3 h	 (57)[a]	1299

	Bu$_3$SnH, AIBN, toluene, reflux, 0.25 h	 (91)	1304
	Bu$_3$SnH, AIBN, toluene, reflux, 0.25 h	 (98)	1304
C$_{12}$			
	Bu$_3$SnH, AIBN, toluene, reflux, 6 h	 (52)	1305
C$_{13}$			
	Bu$_3$SnH, AIBN, toluene, 80°, 6 h	 (37)	1306

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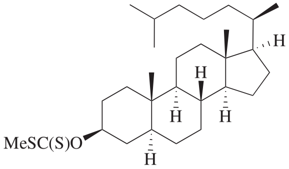
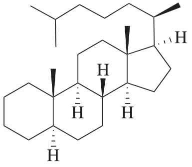
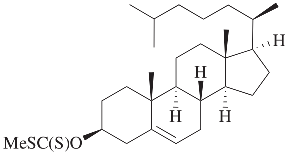
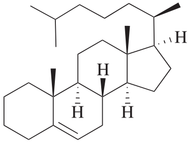
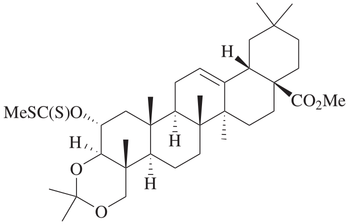
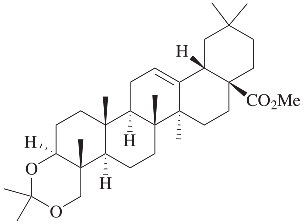
[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

D. SECONDARY ALCOHOLS: STEROIDS AND RELATED SUBSTRATES

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27} 	$(TMS)_3SiH$ (1.2 eq), AIBN (0.1 eq), toluene, 130°, 5 min (flow microreactor)	 (85)	181
	Bu_4NCl, H_3PO_2, Et_3B, air, H_2O, hexane, rt, 3 h	 **I** (77)	200
	PolyHIPE(CTAB)[a], H_3PO_2, toluene, 80°	**I** (100)	204
C_{30} 	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (81)	1307

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[a] This reagent is a macroporous polymer supporting a quaternary ammonium salt.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

E. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES

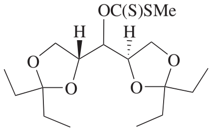
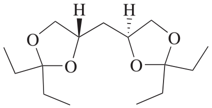
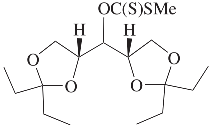
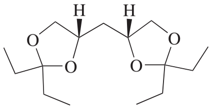
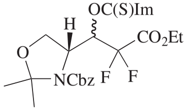
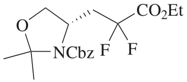
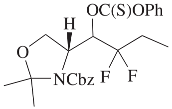
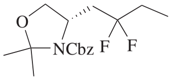
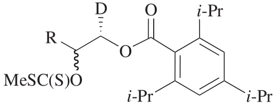
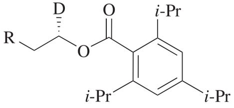
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (95)	1308
	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (81)	1308
	Et_3SiH, Bz_2O_2, dioxane, reflux	 (82)	1309
C_6			
	Et_3SiH, Bz_2O_2, dioxane, reflux	 (82)	1310
C_8			
	$(TMS)_3SiH$, AIBN, toluene, 90°	 R: n-C_6H_{13} (69) R: Ph (78)	1311

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

E. SECONDARY ALCOHOLS: ACYCLIC SUBSTRATES (*Continued*)

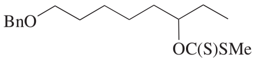
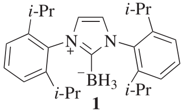
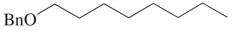
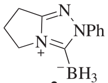
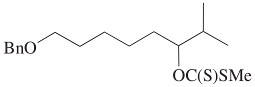
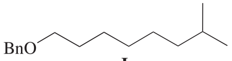
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	**1** (2 eq), AIBN (2 eq), benzene, reflux, 10 h  **1**	 (65) **I**	213
	1 (2 eq), Et_3B (2 eq), O_2, benzene, rt, 2 h	**I** (84)	213
	2 (2 eq), AIBN (0.5 eq), benzene, reflux, 2 h  **2**	**I** (70) + SM (20)	213
C_9 	**1** (2.5 eq), AIBN (2 eq), benzene, reflux, 2 h	 + SM **I**	213
	2 (2 eq), AIBN (*x* eq), benzene, reflux	**I** (64) *x* Time (h) **I** SM 0.5 2 (63) (20) 0.2 4 (67) (20)	213
	2 (1 eq), Et_3B (1 eq), benzene, rt, 2 h	**I** (75)	213
	1 (*x* eq), Et_3B (*y* eq), O_2, benzene, rt, 2 h	**I** + SM *x* *y* **I** SM 1 1 (80) (—) 1 0.2 (79) (—) 0.5 0.5 (71) (21)	213

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

F. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES

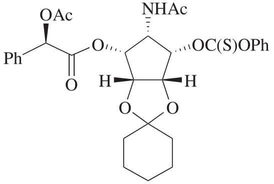
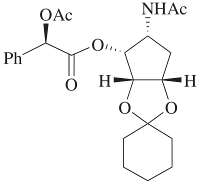
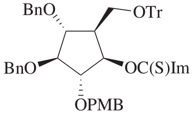
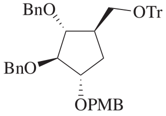
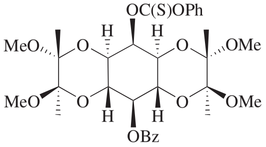
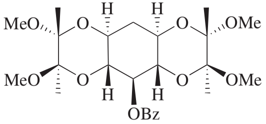
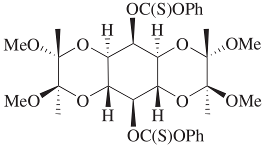
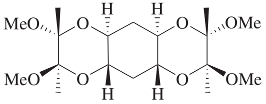
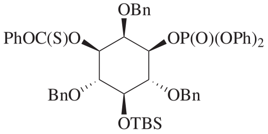
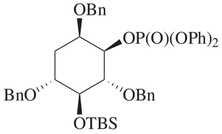
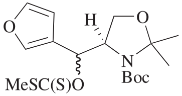
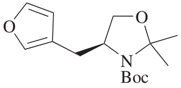
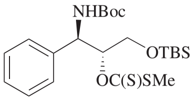
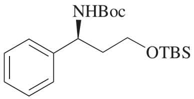
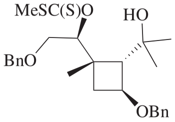
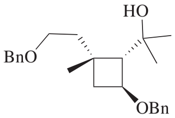
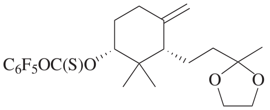
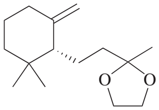
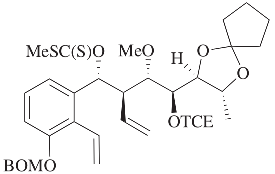
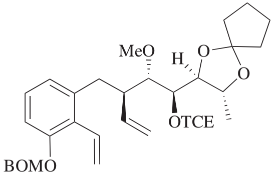
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_5$			
	Bu_3SnH, AIBN, toluene, reflux, 2 h	 (78)	1312
C$_6$			
	Bu_3SnH, AIBN, toluene, reflux, 1 h	 (94)	1313
	Bu_3SnH, AMBN, toluene, reflux, 2.5 h	 (91)	1314
	Bu_3SnH, AMBN, toluene, reflux, 2.5 h	 (84)	1314
	Bu_3SnH, AIBN, toluene, reflux	 (70)	1315

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

F. SECONDARY ALCOHOLS: MONOCYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Bu_3SnH, AIBN, toluene, reflux	 (49)	1316
C_9 	Bu_3SnH, AIBN, toluene, reflux, 6 h	 (81)[a]	1317
C_{10} 	Bu_3SnH, Et_3B, benzene, rt	 (78)	1318
C_{13} 	Bu_3SnH, AIBN, benzene, reflux, 4 h	 (92)	1319
C_{17} 	Bu_3SnH, Et_3B, O_2, toluene, 50°	 (34)[b]	1320

[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

[b] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

G. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES

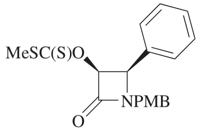
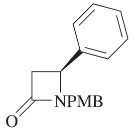
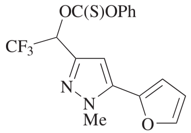
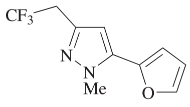
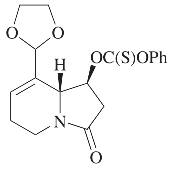
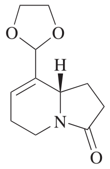
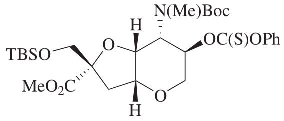
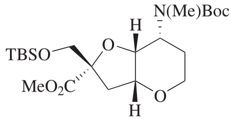
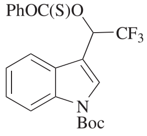
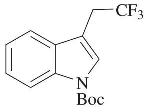
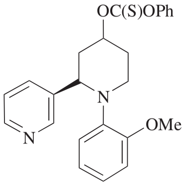
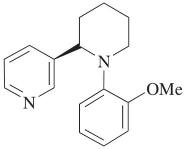
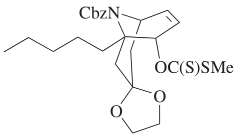
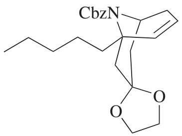
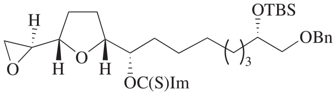
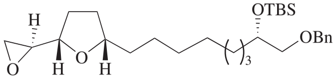
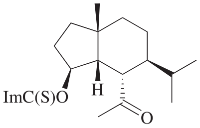
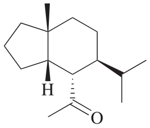
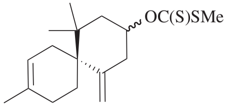
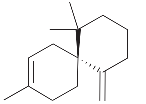
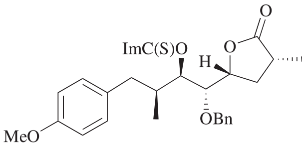
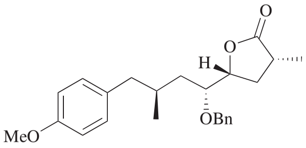
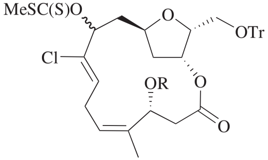
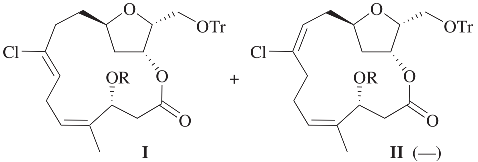
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	Bu_3SnH, AIBN, toluene, reflux, 3–4 h	 (92)	1321
	Bu_3SnH, AIBN, toluene, 80°	 (75)	1322
	Bu_3SnH, AIBN, benzene, reflux	 (94)[a]	1323
	Bu_3SnH, AIBN, toluene, reflux	 (79)	1324
C_{10}			
	Bu_3SnH, AIBN, benzene, reflux, 2 h	 (—)	1325

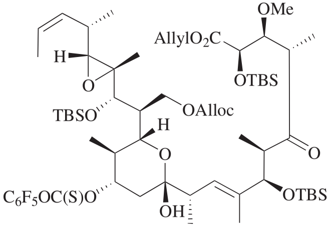
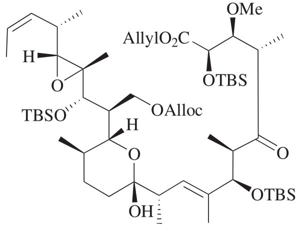
TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

G. SECONDARY ALCOHOLS: BICYCLIC SUBSTRATES (*Continued*)

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		Bu_3SnH, AIBN, benzene, 80°, 24 h	 (67)[a]	1326
C_{13}		Bu_3SnH, AIBN, toluene, reflux	 (75)	1327
C_{15}		$(TMS)_3SiH$, AIBN, benzene, reflux	 (91)[a]	1328
		Bu_3SnH, AIBN, toluene, reflux	 (76)	1329
		Bu_3SnH, AIBN, benzene, reflux, 2 h	 (76)	1330

C$_{16}$		Bu_3SnH, AIBN, benzene, reflux, 2 h		(80)	1331
		Bu_3SnH, AIBN, toluene	 **I** + **II** (—)		1332

R	Temp (°)	**I**
TBS	reflux	(35)
TBS	80	(55)
TBS	60	(53)
Ac	75	(41)

C$_{31}$		Bu_3SnH, Et_3B, toluene, rt		(50)	1333

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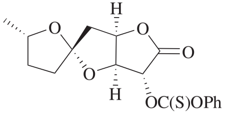
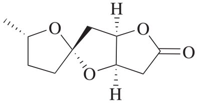
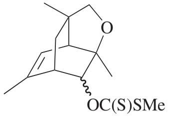
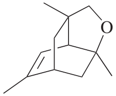
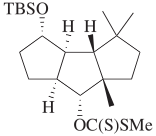
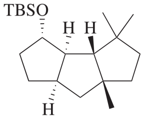
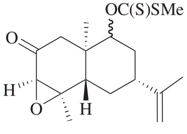
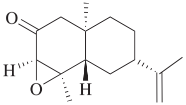
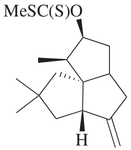
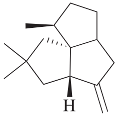
[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

H. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (85)[a]	1334
C_{12} 	Bu_3SnH, AIBN, toluene, reflux	 (81)[a]	1335
C_{14} 	Bu_3SnH, AIBN, toluene, reflux	 (62)[a]	1336
C_{15} 	Bu_3SnH, AIBN, toluene, reflux, 20 min	 (91)	108
	$(TMS)_3SiH$, AIBN, benzene, reflux, 2 h	 (57)	1337

C_{20}

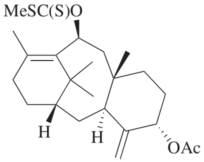
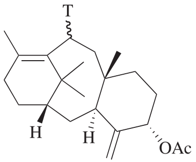
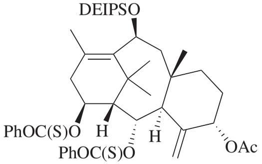
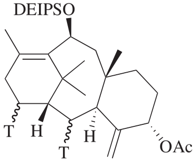
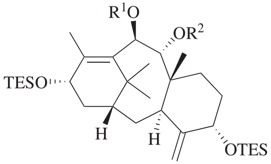
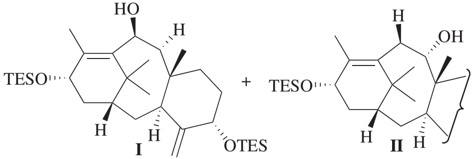
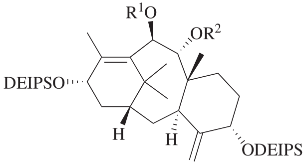
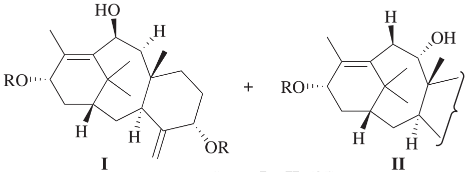
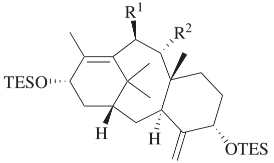
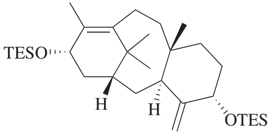
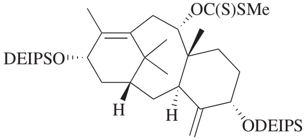
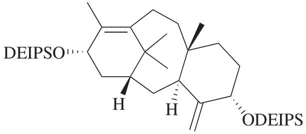
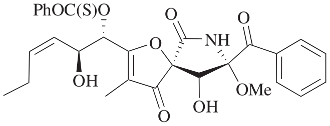
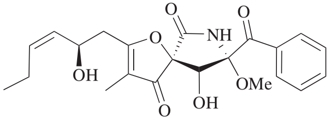
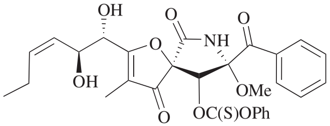
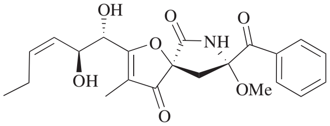
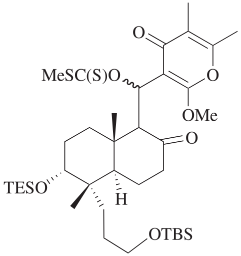
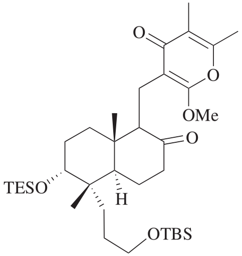
	Bu_3SnT, AIBN, toluene, reflux, 3 h	 (22)	1338
	Bu_3SnT, AIBN, toluene, reflux, 3 h	 (75)	1338
 R^1 / R^2 H / C(S)SMe C(S)SMe / H	Bu_3SnH, AIBN, toluene, reflux, 3 h	 **I** + **II** (86)	1339
 R^1 / R^2 H / C(S)SMe C(S)SMe / H	Bu_3SnH, AIBN, toluene, reflux, 3 h	 R = DEIPS **I** + **II** (85)	1339

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

H. SECONDARY ALCOHOLS: TRICYCLIC SUBSTRATES (*Continued*)

Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}  R^1 / R^2 H / OC(S)SMe OC(S)SMe / H	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (79)	1339
	Bu_3SnH, AIBN, toluene, reflux, 3 h	 (74)	1339
C_{21} 	Bu_3SnH, AIBN, toluene, 75°	 (46)	1340
	Bu_3SnH, AIBN, toluene, 75°	 (26)	1340

C_{23}		Bu_3SnH, AIBN, toluene, reflux, 1 h		(77)	1341

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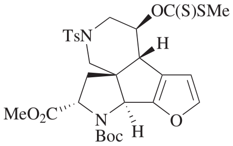
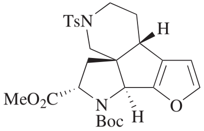
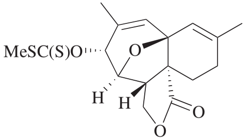
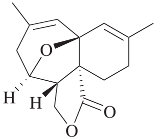
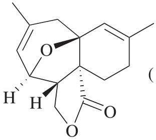
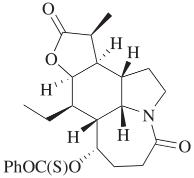
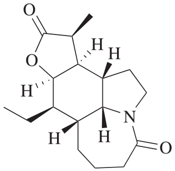
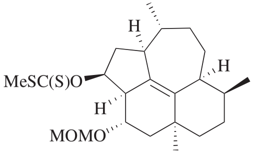
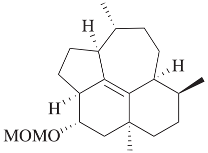
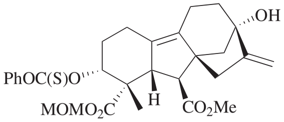
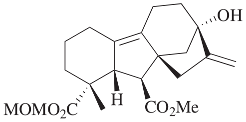
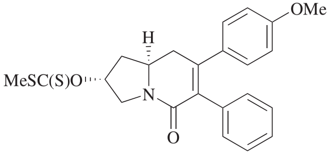
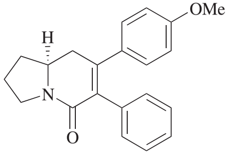
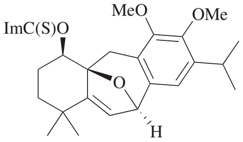
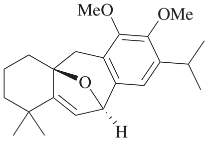
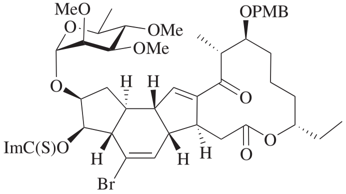
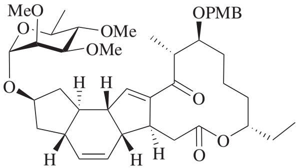
[a] This value is the overall yield for the two-step thioacylation-deoxygenation sequence.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

I. SECONDARY ALCOHOLS: POLYCYCLIC SUBSTRATES

	Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		Bu_3SnH, AIBN, toluene, reflux	 (72)[a]	1342
C_{15}		Bu_3SnH, AIBN, toluene, reflux, 20 min	 (65) +  (15)	1343
C_{17}		Bu_3SnH, AIBN, benzene, reflux, 0.5 h	 (94)	1344
C_{19}		Bu_3SnH, AIBN, toluene, reflux	 (80)	1345

C_{19}		Bu_3SnH, AIBN, toluene, 80°, 3 h	 (84)	1346
C_{20}		Bu_3SnH, AIBN, toluene, reflux, 3 h	 (61)	1347
		Bu_3SnH, AIBN, toluene, reflux, 0.5 h	 (76)[a]	1348
C_{30}		$(TMS)_3SiH$, AIBN, dioxane, 80°	 (68)	250

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[a] This value is the overall yield for a multi-step sequence including the deoxygenation step, but not necessarily the thioacylation step.

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

J. TERTIARY ALCOHOLS (*Continued*)

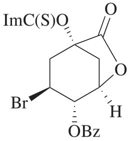
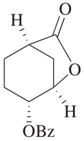
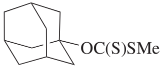
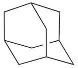
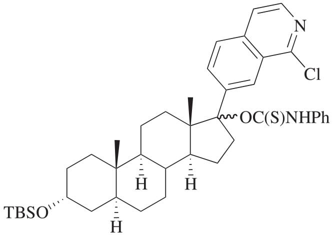
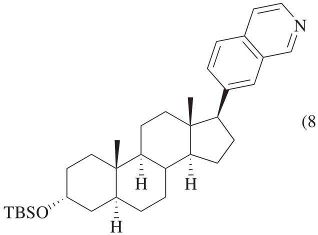
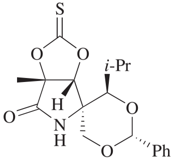
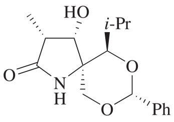
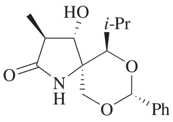
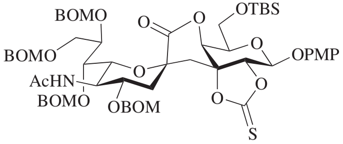
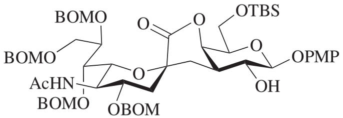
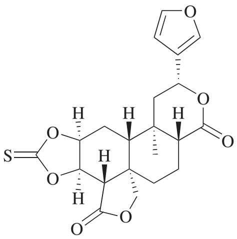
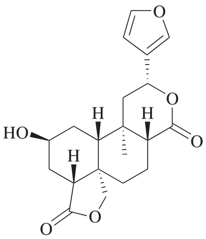
Thioacyl Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Bu_3SnH, AIBN, toluene, reflux	 (56)	1349
C_{10} 	$(TMS)_3SiH$ (1.2 eq), AIBN (0.1 eq), toluene, 130°, 5 min (flow microreactor)	 (77)	181
C_{28} 	Bu_3SnH, AIBN, toluene, 80°	 (81)	1350

TABLE 6. SUPPLEMENTAL TABLE ENTRIES: 2008–2009 (*Continued*)

K. CYCLIC THIOCARBONATES

Cyclic Thiocarbonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Bu_3SnH, AIBN, toluene, reflux	 **I** +  **II** **I** + **II** (95), **I**:**II** = 1:3	1351
C_{16} 	Bu_3SnH, AIBN, toluene, reflux	 (83)	1352
C_{20} 	Bu_3SnH, AIBN, toluene, reflux, 4 h	 (82)	1353

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