CHAPTER 1

THE KRAPCHO DEALKOXYCARBONYLATION REACTION OF ESTERS WITH α-ELECTRON-WITHDRAWING SUBSTITUENTS

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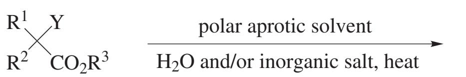
Organic Reactions, Vol. 81, Edited by Scott E. Denmark et al.

ACKNOWLEDGMENTS

We wish to thank Prof. Steven M. Weinreb and the Editors of *Organic Reactions* for numerous helpful suggestions during the preparation of this manuscript. We also greatly appreciate the expert assistance provided by Dr. Danielle Soenen in editing both the text and tables. EC is very grateful to Drs. Linda and Jeff Press for gladly given advice with respect to software problems. One of the authors (APK) would like to acknowledge the contributions of the undergraduate and graduate students at the University of Vermont who were involved in the study of the dealkoxycarbonylation method.

INTRODUCTION

Malonates and other α-activated esters, such as β-keto esters and α-cyano esters, are versatile intermediates in organic synthesis because the acidic nature of their α-hydrogens permits them to undergo a variety of reactions, such as alkylation, electrophilic hydroxylation and amination, or the Michael and Knoevenagel reactions. In many synthetic schemes the removal of the activating ester group then becomes necessary at some point. This transformation can be done by conventional hydrolysis followed by thermal decarboxylation and re-esterification in the case of malonates. However, procedures are available that accomplish this process in one step and under conditions that tolerate the presence of a variety of functional groups and protecting groups. The subject of this chapter is the most widely used of these methods, which involves heating the substrates in a polar aprotic solvent, such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), or hexamethylphosphoric triamide (HMPA), usually in the presence of small amounts of water and/or an inorganic salt (Eq. 1). The process is variously referred to as the Krapcho reaction or Krapcho dealkoxycarbonylation. Several previous reviews,[1–4] book chapters,[5–13] and journal articles[14,14a] have dealt with synthetic applications and mechanistic aspects of the Krapcho dealkoxycarbonylation reaction. Other closely related methods that have found synthetic applications in dealkoxycarbonylations are discussed in the Comparison with Other Methods section and are included in the Tabular Survey with the exception of the palladium-catalyzed dealkoxycarbonylation of activated allyl and benzyl esters, which is briefly mentioned in the former but is not included in the latter. Occasionally reference is made in the subsequent sections to entries in the tables; these take the form (Table number-carbon-count-reference).



(Eq. 1)

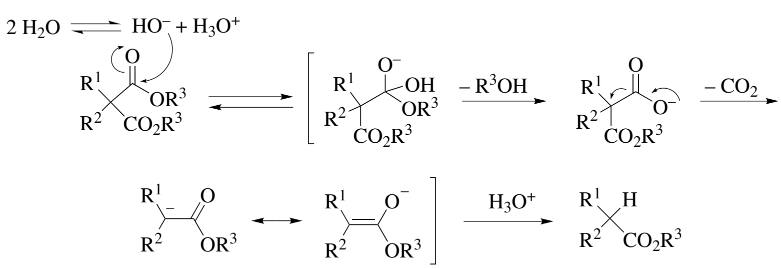
$Y = CO_2R^4$, COR^5, CN, NO_2, SO_2R^6

MECHANISMS

The mechanism of the Krapcho dealkoxycarbonylation reaction depends on the structure of the substrate and whether or not inorganic salts are added.

Dealkoxycarbonylations in Polar Aprotic Solvents in the Presence of Water

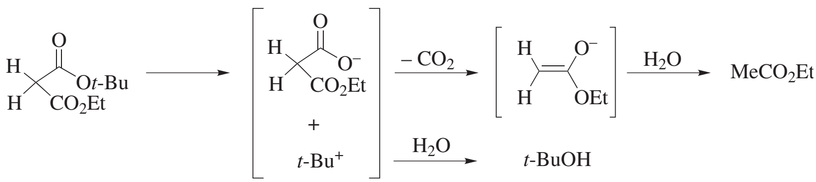
The dealkoxycarbonylation of α-monosubstituted malonates, β-keto esters, and α-cyano esters in hot polar aprotic solvents containing water is believed to proceed by the $B_{AC}2$/decarboxylation mechanism shown in Scheme 1. This supposition is based on the observation that the ratio of $k(H_2O)/k(D_2O)$ for the



Scheme 1

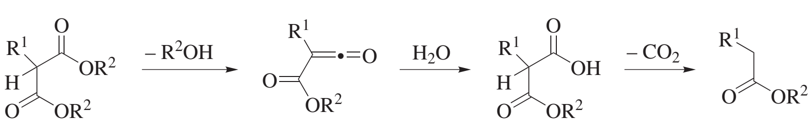
dealkoxycarbonylation of diethyl phenylmalonate in DMSO is about 2.7.[15] A similar mechanism has been proposed for the water-catalyzed nucleophilic attack at the carbonyl group for related aryl-substituted dichloroacetates.[16] Furthermore, a competition experiment with a 1:1 mixture of dimethyl malonate and diethyl malonate in wet DMF (microwave irradiation, 180°, 2 to 20 minutes) results in only a slight preference (ca. 1.1:1) for dealkoxycarbonylation of the dimethyl ester, indicating that direct attack of water on the alkyl group is of little or no importance.[17]

Esters in which an oxygen$_{alkyl}$–carbon bond cleavage leads to a stabilized carbocation, such as *tert*-butyl, benzyl, or allyl esters, may preferentially react by an initial S_N1-type alkyl–oxygen bond cleavage as shown in Scheme 2. Thus, heating *tert*-butyl ethyl malonate in refluxing DMSO/H_2O for 4 hours produces a mixture in which the ethyl ester predominates by a ratio of 10:1, indicative of a chemoselective de-*tert*-butoxycarbonylation.[18]



Scheme 2

A possible alternative mechanistic pathway for dealkoxycarbonylations of substrates with at least one α-hydrogen is the initial formation of a ketene intermediate (Scheme 3). However, the suggestion has been made that such a mechanism can be excluded because diethyl benzylmalonate is not deethoxycarbonylated in dry DMF, whereas in DMF containing water it is. Moreover, no intermediate ketene is trapped when heating this ester in dry DMF in the presence of dihydropyran or cyclohexanone.[17] Injection of methyl α-ethylacetoacetate into a GC–FTIR instrument at an injection temperature of 240–280° does produce the absorption at 2121 cm^{-1}, indicative of a ketene. Under similar conditions, methyl α,α-dimethylacetoacetate does not exhibit this absorption.[19] However, the relevance of this thermolysis procedure to the hydrolysis mechanism is questionable.



Scheme 3

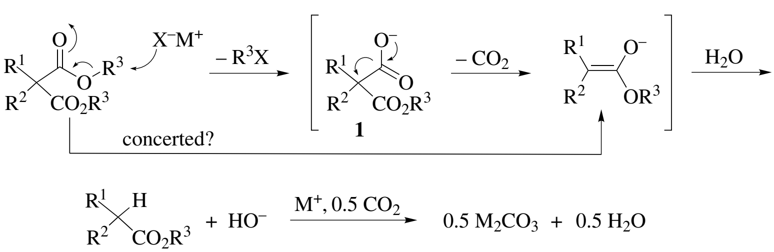
Dealkoxycarbonylations in Polar Aprotic Solvents in the Presence of Water and Inorganic Salts

Although a number of activated esters undergo dealkoxycarbonylations in polar aprotic solvents in the presence of water alone, α,α-disubstituted malonates are resistant under these conditions, and the addition of salts such as NaCN, NaI, or LiCl is necessary in these cases.[1,2] Some α-monoalkylmalonates also require the addition of inorganic salts to enhance the reaction rates.[15,20] The nitrile/alcohol ratios for several malonate dealkoxycarbonylations with potassium cyanide and wet DMSO are tabulated in Eq. 2.[15]

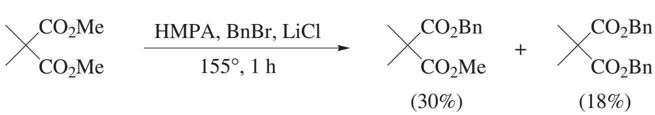
(Eq. 2)

R^1	R^2	R^3	R^3CN/R^3OH
Et	H	Et	28:72
Me	H	Et	33:67
Me	Me	Et	58:42
Et	Et	Et	81:19
Et	Et	Me	100:0

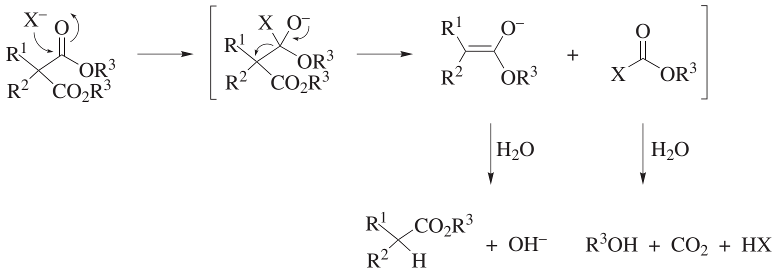
The formation of acetonitrile and no methanol in the case of dimethyl α,α-diethylmalonate (Eq. 2) suggests a dominant $B_{AL}2$ route involving initial attack of cyanide at the carbon of the ester *O*-alkyl group followed by decarboxylation and protonation (Scheme 4). There appears to be no experimental evidence to distinguish between this and a concerted mechanism. Intermediate **1** has been trapped with benzyl bromide in one example (Eq. 3).[21] The reactions of monosubstituted malonates give much lower nitrile/alcohol ratios (Eq. 2), indicative of a competitive $B_{AC}2$ pathway (Scheme 5). The deuterium isotope effect for the dealkoxycarbonylation of diethyl phenylmalonate in the presence of lithium chloride or potassium cyanide is $k(H_2O)/k(D_2O) = 1.09$ and 1.10, respectively,[15] indicating that water does not compete effectively in the $B_{AC}2$ mechanism.



Scheme 4

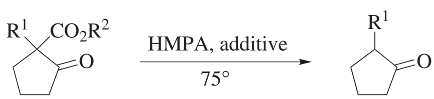


(Eq. 3)



Scheme 5

The relative rates of the dealkoxycarbonylation of keto esters **2** (R^1 = Bn) with sodium cyanide in HMPA (Eq. 4) are 249:4:1:1 for the methyl, ethyl, isopropyl, and *tert*-butyl esters, respectively,[22] providing further evidence for the $B_{AL}2$ mechanism. Cyanide is about 26 and 64 times more efficient than chloride and bromide, respectively, in the dealkoxycarbonylation of the methyl ester **2** (R^1 = Bn, R^2 = Me).[22]



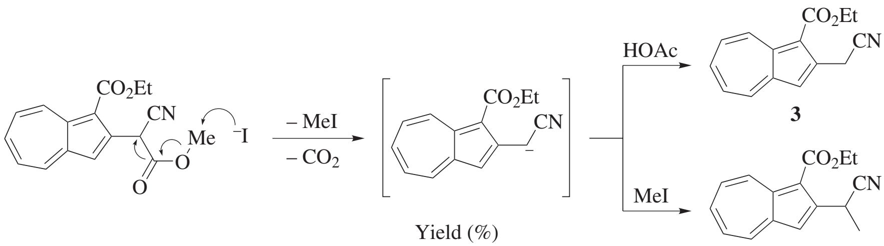
(Eq. 4)

2

R^1	R^2	Additive	Time (h)	Yield
Me	Me	NaCN	1	(70%) + MeCN (70%)
Bn	Me	LiCl	24	(90%)

In dealkoxycarbonylations proceeding by either the $B_{AL}2$ or the $B_{AC}2$ mechanism, one equivalent of hydroxide ion is formed which may react with one-half of the carbon dioxide produced to give carbonate ion. Lithium carbonate is isolated in 30–40% yield (60–80% of theory, see Scheme 4) in a number of dealkoxycarbonylations involving lithium chloride.[15] The other half of the carbon dioxide under this scenario should be evolved as the gas. In the only case where its volume appears to have been measured, only 12.5% (25% of theory) is evolved.[23] A complete mass balance of a Krapcho dealkoxycarbonylation has not been reported. It has been stated occasionally that the Krapcho dealkoxycarbonylation proceeds under essentially neutral conditions. This is true only for the variation that does not involve inorganic salts.

When bromides or iodides are used as metal salts, the alkyl bromides or iodides formed in the dealkoxycarbonylation may alkylate the intermediate enolates or stabilized carbanions (product **4**, Scheme 6).[24] This problem is avoided by addition of one equivalent of acetic acid in order to protonate the carbanion more effectively (product **3**, Scheme 6).



Conditions	Yield (%) 3	4	3/4
DMF, HOAc, LiI•2H_2O, 140°, 1 h	75	0	—
DMF, LiI•2H_2O, reflux, 1.5 h	—	—	38:62

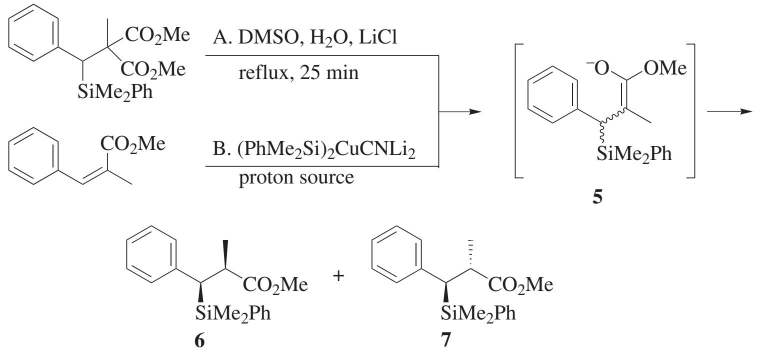
Scheme 6

SELECTIVITY

Diastereoselectivity

Mixtures of diastereomers are to be expected in the dealkoxycarbonylation of activated esters with other resident stereogenic centers. Protonation of the intermediate enolates by an external proton source is expected to occur from the less hindered face. On the other hand, water, which is the proton source in most cases, is relatively small, and the required high temperatures and often extended reaction times may cause equilibration to the thermodynamically more stable isomers and this is frequently observed. Moreover, kinetic selectivity tends to decrease as the reaction temperature increases. Finally, protonation may occur on oxygen as well as carbon. In practice it is usually very difficult to predict whether a particular reaction will proceed under kinetic or thermodynamic control. In most cases epimerization presumably occurs in the product by reversible removal of a proton α to the activating group by either the enolate or the hydroxide ion. Addition of one equivalent of an acid in principle should prevent this, but even though such an expedient has been used to avoid alkylation of the enolate (Scheme 6), it does not appear to have been employed to influence the diastereoselectivity. Another approach that has apparently been used only once (see below under Four-Membered Rings) and that merits further exploration is to use a bulky proton source under anhydrous conditions.

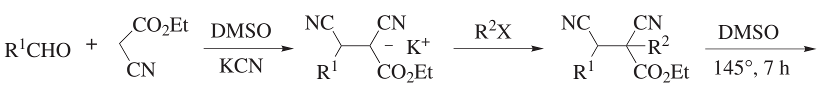
Acyclic Substrates. A fair number of dealkoxycarbonylations of prochiral acyclic activated esters have been reported in the literature, almost exclusively involving α,α-disubstituted malonates (Table 3), but diastereomeric ratios of the products are rarely given. In an interesting comparison, enolate **5** is generated both by a Krapcho dealkoxycarbonylation and a conjugated addition (Scheme 7).[25] Even though the protonation temperatures differ by 267°, the diastereoselectivity is remarkably similar. Using *tert*-butyl alcohol as the proton source in the conjugate addition leads to improved selectivity of diastereomer **6** versus **7**, indicating that protonation occurs from the less hindered side.

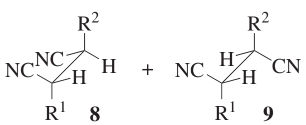


Method	Proton Source	Protonation Temp (°)	Yield (%) 6 + 7	6/7
A	H_2O	189	68	70:30
B	NH_4Cl, H_2O	–78	84	85:15
B	*t*-BuOH	–78	—	93:7

Scheme 7

In the one-pot, three-step synthesis of 1,2-disubstituted succinonitrile diastereomers **8** and **9** shown in Scheme 8,[26] single isomers are obtained when the two substituents are bulky. No explanation for this selectivity has been advanced. The structure assignments rest solely on the fact that crystalline solids rather than oils are obtained in both cases. When both groups are methyl or ethyl, mixtures of unspecified composition are obtained.





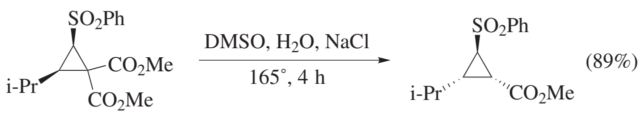
R^1	R^2	X	Yield (%) 8 + 9	8/9
Me	Me	I	23	mixture
Et	Me	I	62	mixture
i-Pr	*i*-Pr	I	61	**8** only
i-Pr	Bn	Cl	53	**8** only
Ph	Me	I	17	mixture

Scheme 8

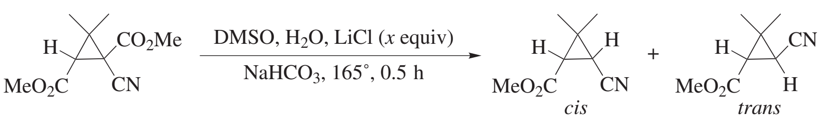
Based on the scarce evidence available, dealkoxycarbonylations of acyclic prochiral activated esters are likely to be highly diastereoselective only in special cases.

Cyclic Substrates. The situation should become somewhat more favorable for the configurationally less flexible cyclic prochiral activated esters, but the possibility of epimerization remains. Although the Krapcho dealkoxycarbonylation has been used extensively with mono-, bi-, and polycyclic substrates, in many cases only a few of a particular structural type are known so that the generalizations offered below are tentative.

Three-Membered Rings. Protonation of the intermediate enolates from the less hindered side should produce the *cis*-isomers from substituted cyclopropane-1,1-dicarboxylic esters, but in practice the *trans*-isomers usually predominate or are formed exclusively, especially if another electron-withdrawing substituent is present as shown in Eq. 5.[27] Complete epimerization in this case may proceed via a ring-opened zwitterion,[27] considering the reluctance of cyclopropyl esters to form enolates.[28] The *cis*-isomer is formed predominantly in the dealkoxycarbonylation of the single example of a prochiral three-membered α-cyano ester, and the *cis*/*trans* ratio depends on the concentration of the lithium chloride used (Eq. 6).[29] Larger amounts of the salt cause a more selective reaction but also decrease its rate. No rationale for these observations has been advanced.



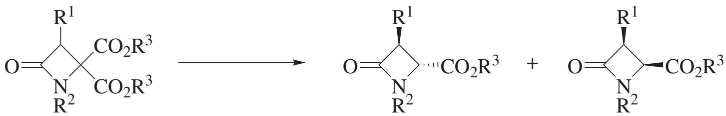
(Eq. 5)



(Eq. 6)

x	Yield (%) *cis* + *trans*	*cis*/*trans*
2	89	2:1
7	64	5:1

Four-Membered Rings. The dealkoxycarbonylation of only two substituted cyclobutane-1,1-diesters was found in the literature. The 2-(4′-bromophenyl) derivative gives exclusively the *trans*-ester whereas the 3-benzyloxy diester gives a mixture of *cis*- and *trans*-isomers (Eq. 61; section on Four-Membered Geminal Diesters). Most reported examples involve β-lactams, which are among the few systems where sufficient data under similar reaction conditions are available for a number of differently substituted prochiral substrates (Eq. 7). Again the *trans*-isomers usually predominate except for the phenylthio-substituted β-lactam. Unfortunately the reaction temperature is ambiguous in this case; the lower number is quoted in the discussion, the higher in the experimental section. With regard to the last entry, it is believed that the intramolecular protonation by the CF_3CONH group is responsible for the high *trans*-selectivity even though water is present. The *trans/cis*-selectivity for the less acidic CbzNH-analog is 25:1, and 1.25:1 for the phthaloyl analog where water becomes the protonating agent.[33] A similar intramolecular protonation by an AcNH-group producing a dr of 20:1 has been reported for two carbohydrate diesters (4D-C_{14}).[34]



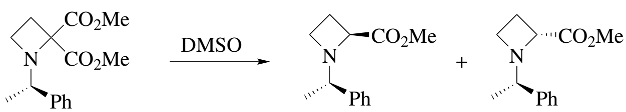
trans *cis*

(Eq. 7)

R^1	R^2	R^3	Conditions	Yield (%) *trans* + *cis*	*trans*/*cis*	Refs.
PhO	4-$MeOC_6H_4$	Et	DMF, LiCl, 140°,[b] 8 min	64	1:1	30
BnO	4-$MeOC_6H_4$	Et	DMF, LiCl, 140°,[b] 8 min	79	2:1	30
PhS	4-$MeOC_6H_4$	Et	DMSO, H_2O, NaCl 189°(140°), 4 h	81	1:12	31
i-Pr	2,4-$(MeO)_2C_6H_3CH_2$	Et	DMSO, H_2O, NaCl, 180°	85	9:1	32
$CF_3CONH(CH_2)_3$[a]	2,4-$(MeO)_2C_6H_3CH_2$	Me	DMF, H_2O, LiCl, 130°, 3.5 h	93	46:1	33

[a] The (*R*)-enantiomer was used.
[b] The reaction mixture was heated using microwave irradiation.

Dealkoxycarbonylation of the azetidine diester **10** under anhydrous conditions with the bulky 2,6-di-*tert*-butyl-4-methylphenol or (*S*)-binaphthol as the proton source gives the diasteromers **11** and **12** in a ratio of 73:27 and 74:26, respectively (Eq. 8).[35] The ratio obtained with water as the proton source was not reported. Generating the intermediate enolate with LDA in THF and protonation with methanol at −78° results in a 87:13 mixture of isomers **11** and **12**. Attempted equilibration of the two esters with sodium methoxide or DBU in refluxing methanol is unsuccessful. These results are believed to indicate that the dealkoxycarbonylation proceeds under kinetic control. Protonation from the *re* face of one of the two preferred enolate conformers is believed to be responsible for the observed diastereoselectivity.[35]

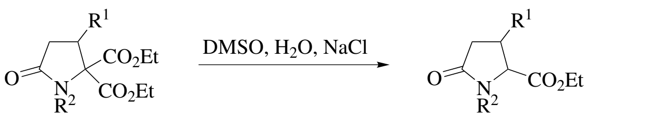


10 **11** **12**

(Eq. 8)

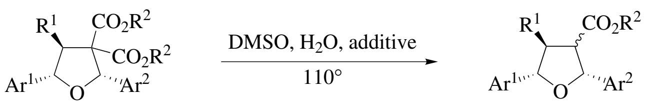
Conditions	Yield (%) **11 + 12**	**11/12**
H_2O, NaCl, 160°	65	—
2,6-$(t\text{-}Bu)_2$-4-MeC_6H_2OH, LiCl (3 equiv), 3 Å MS, 140°, 2 h	78	73:27
(*S*)-binaphthol, LiCl, 3 Å MS	23	74:26

Five-Membered Rings. The dealkoxycarbonylation of only one prochiral five-membered carbocyclic diester was found in the literature. Dimethyl 2-benzylcyclopentanedicarboxylate gives a dr of 84:16, but no structure assignments were made.[36] The two prochiral pyrrolidinone 1,1-diesters shown in Eq. 9 give contradictory results even though the steric bulk of the directing α-substituents is similar. The dealkoxycarbonylation of the furan derivative shown in the second entry of Eq. 10 is highly diastereoselective, which in this case is a consequence of intramolecular protonation of the intermediate enolate by a neighboring carboxy group. The reaction becomes nonselective when the corresponding benzyl ester is used. When the carboxy group is absent, the *trans*-isomer predominates, presumably by epimerization of the initially formed *cis*-isomer. The carboxylate product of entry 2 may be protected from epimerization by the reluctance to form a dianion.



(Eq. 9)

R^1	R^2	Temp (°)	Time (h)	Yield (%)	*cis*/*trans*	Refs.
4-ClC_6H_4	Boc	150	40	100	67:33	37
$EtO_2C(CH_2)_6$	Me	189	2	84	0:100	38

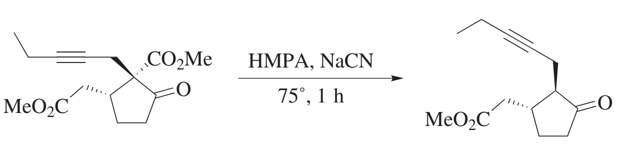


(Eq. 10)

R^1	R^2	Ar^1	Ar^2	Additive	Time (h)	Yield (%)	*cis*/*trans*[a]	Refs.
H	Me	Ph	Ph	NaCN	20	75	13:87	39
HO_2C	Et	3,4-$(MeO)_2C_6H_3$	3,4-$(OCH_2O)C_6H_3$	KOAc	16	72	>95:5	40

[a] *Cis*/*trans* refers to the relationship of CO_2R^2 to Ar^2.

Prochiral five-membered cyclic β-keto esters produce the *trans*-isomers predominantly or exclusively irrespective of the nature of the α-substituents, even when the reaction is carried out under rather mild conditions (Eq. 11).[41] This presumably reflects the more ready epimerization of ketones compared to esters.



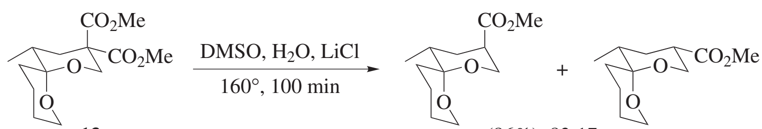
(84%) (Eq. 11)

Six-Membered Rings. Little is known about carbocyclic geminal diesters beyond the observation that dealkoxycarbonylation of diethyl 3- and 4-methylcyclohexane-1,1-dicarboxylates as well as of the 4-*tert*-butyl analog (Eq. 12, entry 6) gives 1:1 mixtures of the *cis*- and *trans*-monoesters, whereas in the case of the 2-methyl analog a slight preference for protonation from the equatorial side results in a 60:40 mixture of the *cis*- and *trans*-products.[42] By comparison, the thermodynamic *cis*/*trans* ratio for the 4-*tert*-butyl analog is 15:85. Introduction of one oxygen into the six-membered ring (Eq. 12, entry 5), and especially of two oxygens (entries 1, 2, and 4) causes predominant formation of the *cis*-isomers by protonation from the equatorial side. The experiments of entries 1 and 2 are carried out under kinetic control with no change in composition over time. However, when the temperature in entry 2 is increased to 148–153°, the amount of the *cis*-isomer gradually decreases at the expense of the thermodynamically more stable *trans*-isomer. Epimerization of the product mixture of entry 4 with sodium methoxide in methanol gives an equilibrium mixture that contains 16% of the *cis*- and 84% of the *trans*-isomer. The methyl and ethyl esters in entries 1 and 2 show the same diastereoselectivity and changing the solvent to DMF has no effect on the product ratio. The influence of the ring oxygens on the diastereoselectivity has been explained on the basis of frontier molecular orbital theory, which predicts accumulation of negative charge in the enolate in the equatorial direction.[43] Similar results are obtained with the spiroketal **13** (Eq. 13).[47] In this reaction the enolate of the product ester was also generated with LDA at −78°; treatment with methyl iodide or PhSeBr proceeds again predominantly by attack from the equatorial side to give *cis*/*trans* mixtures in the ratios of 86:14 and 90:10, respectively.

cis *trans*

R^1	R^2	Y	Z	Additive	Temp (°)	Time (h)	Yield (%) *cis* + *trans*	*cis*/*trans*	Refs.
i-Pr	Me	O	O	LiCl, py	135	3–4	—	86:14	43
i-Pr	Et	O	O	LiCl, py	135	3–4	—	86:14	43
i-Pr	Me	O	O	NaCl	189	7	77	26:74	44
t-Bu	Me	O	O	LiCl	140–145	4	80	89:11	45
MeO	Me	CH_2	O	NaCl	150	10	81	56:44	46
t-Bu	Et	CH_2	CH_2	LiCl	194	4	62	49:51	42

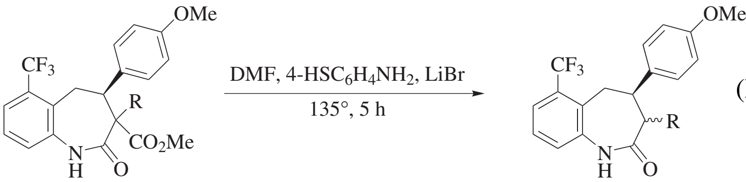
(Eq. 12)



(Eq. 13)

13 (86%) 83:17

Seven-Membered Rings. The only relevant available data are for the α-alkoxycarbonyl lactams **14** (Eq. 14),[48] where protonation of the intermediate amide enolate from the less hindered side should give the *cis*-isomers. This is true for the methyl analog but with increasing bulk of the R substituent increasing amounts of the *trans*-isomers are formed. No rationale for this observation has been advanced. The aminothiophenol is added to trap the methyl bromide that otherwise causes partial *N*-methylation of the products. Interestingly, this problem is less severe when lithium bromide is replaced by lithium iodide even though methyl bromide with its lower boiling point should escape more readily from the reaction medium at the elevated temperature.

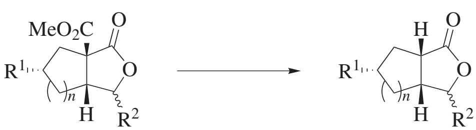


14

(Eq. 14)

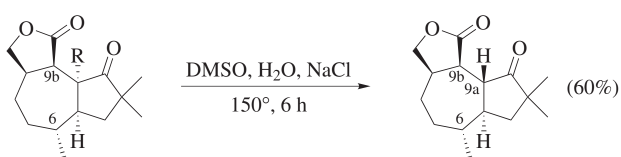
R	Yield (%)	*cis*/*trans*
Me	93	95:5
Et	100	90:10
allyl	85	87:13
Bn	100	50:50

Polycyclic Systems. Dealkoxycarbonylation of β-keto esters and α-alkoxycarbonyl lactones in the bicyclo[3.3.0] and bicyclo[4.3.0] series with the ester groups on the ring junction give the *cis*-fused products (Eq. 15). Only a few examples of the Krapcho dealkoxcarbonylation of the corresponding bicyclo [4.4.0] substrates are known and they either give exclusively (6B-C_9;[51] 11B-C_{18}[52]) the *cis*-isomers or predominantly (11B-C_{12})[53,54] the *trans*-fused product, which in this case is the thermodynamically less stable isomer. Two reports concerning bicyclo[5.3.0] systems can be found in the literature: in one case the *trans*-fused product is formed exclusively, albeit in low yield (11A-C_{14})[55], in the other the product structures depend on the substitution patterns (Eq. 16).[56] When the configurations at C-6 and C-9b are reversed, the *cis*-fused ketone is obtained. The products in both cases are not the ones of protonation from the less hindered side, indicating thermodynamic control.



(Eq. 15)

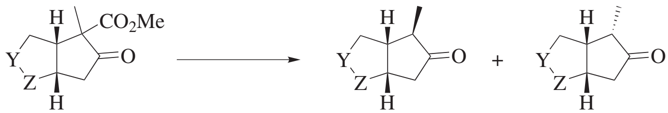
n	R^1	R^2	Conditions	Yield (%)	Refs.
1	TBSO	H	DMSO, H_2O, LiCl, 140°, 12 h	99	49
2	H	Me	HMPA, NaCN, 100°, 12 h	69	50



R = CO_2Me

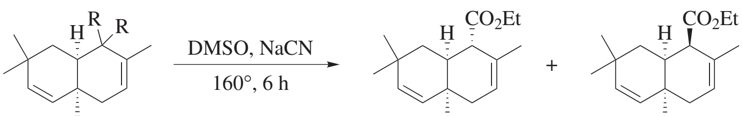
(Eq. 16)

Dealkoxycarbonylations of *cis*-fused [$x.y$.0]bicyclic substrates where the ester function is not on the ring junction should occur by kinetic protonation from the less hindered convex sides of the molecules to give the *endo*-isomers. In practice the thermodynamically more stable *exo*-isomers are formed predominantly or exclusively (Eqs. 17 and 18[59]).



exo *endo* (Eq. 17)

Y	Z	Conditions	Yield (%) *exo* + *endo*	*exo*/*endo*	Refs.
O	CO	DMF, H_2O, LiCl, reflux, 1 h	64	100:0	57
CO	CH_2	DMSO, H_2O, NaCl, reflux, 5 h	69	73:27	58

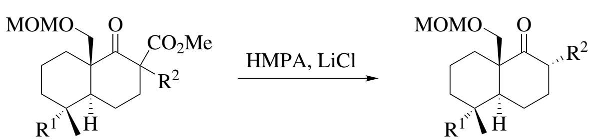


(Eq. 18)

R = CO_2Et *exo* *endo*

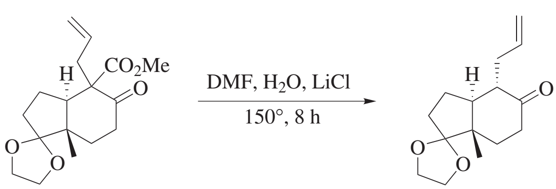
exo + *endo* (70%), *exo*/*endo* = 89:11

β-Keto esters in the *trans*-fused bicyclo[$x.y.0$] series also produce the more stable equatorial isomers (Eqs. 19 and 20[62]) under thermodynamic control. The product in entry 1 of Eq. 19 is stable to heat and base. Dealkoxycarbonylation of 1,1-diesters and α-cyano esters in this series, on the other hand, furnish mixtures (Eq. 21;[63] 4D-C_{18}[64]) where in the case of the α-cyano esters the less stable quasi-axial product predominates. In Eq. 21 the quasi-axial ester **15** (R = CO_2Me) has been epimerized completely to the quasi-equatorial ester **16** by the action of sodium methoxide.

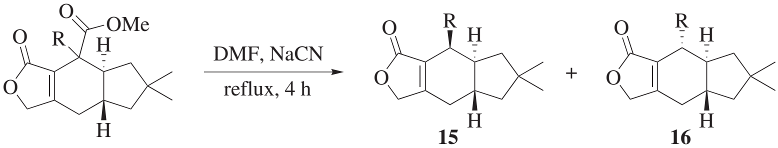


(Eq. 19)

R^1	R^2	Temp (°)	Time (h)	Yield (%)	Refs.
Me	$MeCO(CH_2)_2$	120–140	8	84	60
$Me_2C{=}CH(CH_2)_2$	Me	130	2	92	61



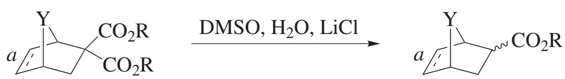
(99%) (Eq. 20)



15 16 (Eq. 21)

	Yield (%)	
R	**15 + 16**	**15/16**
NC	63	2:1
MeO_2C	70	1:2

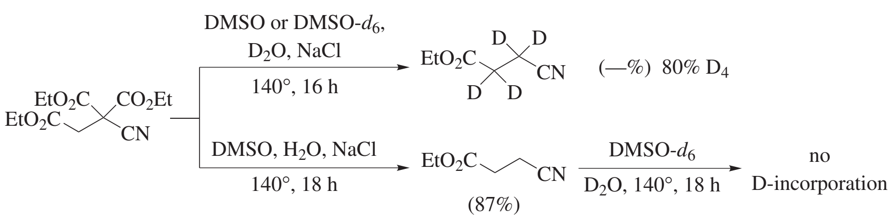
Dealkoxycarbonylation of activated esters in bicyclo[$x.y.1$] systems usually occurs by protonation of the intermediate enolates preferentially (Eq. 22; 4C-C_{17};[65] 4D-C_{18-22}[66]) or exclusively (4C-C_{14})[67] from the less hindered *exo*-side to give the *endo*-products. The thermodynamic equilibria for the products of entries 2 and 3 in Eq. 22, determined for the methyl rather than the ethyl esters, are *exo*/*endo* = 70:30 and 48:52, respectively.[68]



(Eq. 22)

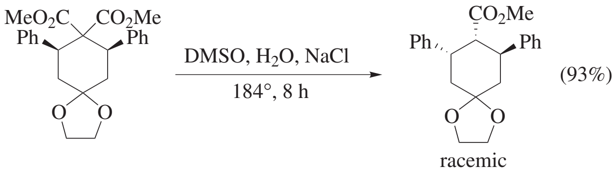
Bond *a*	Y	R	Temp (°)	Time (h)	Yield (%)	*exo*/*endo*	Refs.
single	O	Me	135	3–4	—	23:77	43
single	CH_2	Et	185	4	63	31:69	42
double	CH_2	Et	193	1	22	20:80	42

Epimerization of Neighboring Chiral Centers. Treatment of triethyl 1-cyanoethane-1,1,2-tricarboxylate under Krapcho conditions produces first an α-cyano ester and finally ethyl 3-cyanopropanoate in a second dealkoxycarbonylation (Scheme 9).[69] When the reaction is carried out in the presence of deuterium oxide, deuterium is introduced to a considerable extent in both the 2- and the 3-positions. No deuterium is incorporated into ethyl 3-cyanopropanoate under these conditions, indicating that exchange in both positions occurs in the substrate or in the intermediate α-cyano ester in competition with dealkoxycarbonylation. It is thus not surprising that epimerization of chiral centers α to the activated ester undergoing dealkoxycarbonylation is observed on occasion.

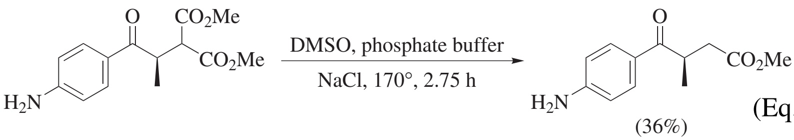


Scheme 9

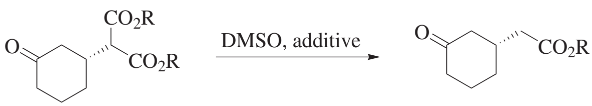
In most of the reported examples the α-carbon carries an anion-stabilizing substituent such as phenylsulfonyl (Eq. 5), phenyl (Eq. 23;[70] 11B-C_{19}[71]), or benzoyl (Eq. 24).[72] In the case of Eq. 24, standard Krapcho conditions (DMSO, H_2O, NaCl, 160°) cause "significant loss" of enantiomeric purity, whereas in the presence of a phosphate buffer there is "no significant loss," although the product yield is rather low. The racemizations in entries 2–4 of Eq. 25 have been attributed to a retro-Michael reaction/Michael addition sequence of malonate ion.[74] The α-carbon in the keto ester shown in Eq. 26 carries no anion-stabilizing group;[75] the mechanism of racemization in this case may involve a reversible aza-Michael reaction.



(Eq. 23)

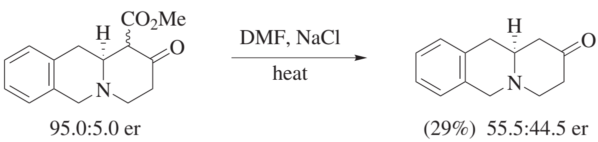


(Eq. 24)



(Eq. 25)

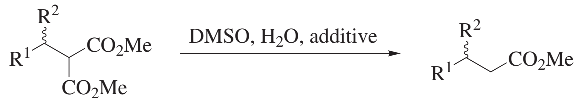
R	er	Additive(s)	Temp (°)	Time	Yield (%)	er	Refs.
Me	>99.5:0.5	LiI•3H_2O	180	25 min	52	99.5:0.5	73
Me	91.5:8.5	LiI, H_2O	170	1 h	34	89.5:10.5	74
Et	96.5:3.5	NaCl, H_2O	175	3 h	36	93.0:7.0	74
Et	96.5:3.5	LiCl, H_2O	170	3 h	42	68.5:31.5	74



(Eq. 26)

These cases comprise most of the racemizations of non-racemic chiral α-carbons during a Krapcho dealkoxycarbonylation found in the literature, although the enantiomeric ratios of the products are frequently not given. In the majority of reactions where such data are available, the enantiomeric purity is not or only somewhat compromised. Examples include the synthesis of chiral non-racemic β-amino esters and their derivatives (Eq. 27), and the preparation of ester **17** (Eq. 28).[80] The enantiomeric purity was established in a subsequent product.

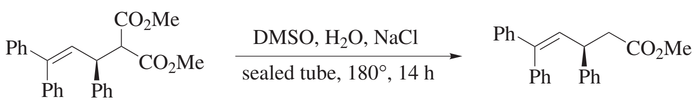
Of note in Eq. 27 is the formation of the free amine from the α-amino malonate hydrochloride. Perhaps efficient protonation of the intermediate enolate by the amine salt is responsible for the high enantiomeric purity of the product.



(Eq. 27)

R^1	R^2	er	Config.	Additive	Temp (°)	Time	Yield (%)	er	Refs.
Me	$NH_3^+Cl^-$	—	(*S*)	NaCl	reflux	2 h	86[a]	97.5:2.5	76
t-BuSCOCH$_2$	NHBz	88.0:12.0	(*R*)	—	150	20 h	65	80.0:20.0	77
Ph	NHCO$_2$Et	96.5:3.5	(*R*)	—	160[b]	10 min	80	92.5:7.5	78
Ph	NHBz	81.5:18.5	(*R*)	—	180	12 h	91	81.5:18.5	79

[a] The product was the free amine.
[b] Microwave irradiation was used.



97.5:2.5 er

17 (79%) ≥97.0:3.0 er

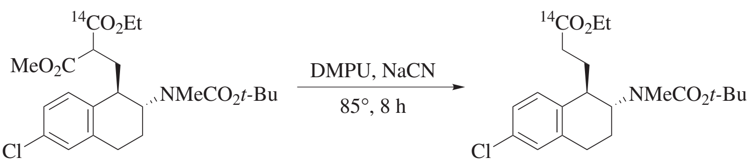
(Eq. 28)

The Krapcho dealkoxycarbonylation has been used in a number of reactions to determine the enantiomeric purity of the α-carbon in the precursor. Although this may be valid in many cases, caution is advisable in view of what is discussed above.

Chemoselectivity

α-Monosubstituted malonates have been selectively dealkoxycarbonylated in the presence of α,α-disubstituted ones with water in DMSO under microwave irradiation.[17] The reaction was carried out on a mixture of the two types of malonates but no example where the two functional groups occur in the same molecule has been reported.

As mentioned in the Mechanisms section, methyl esters are dealkoxycarbonylated more readily than ethyl esters in the presence of an inorganic salt and this is exploited in a radiochemical synthesis (Eq. 29).[81] A similar selectivity is seen in the dealkoxycarbonylation of a six-membered geminal diester (Scheme 13).

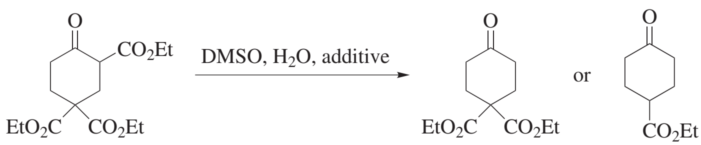


(65%)

(Eq. 29)

Heating a solution of ethyl *tert*-butyl malonate in wet DMSO at reflux gives ethyl acetate and *tert*-butyl acetate in a ratio of 10:1 (Scheme 2). When lithium chloride is added, the ratio decreases to 6:1, indicating that the $B_{AC}2$ mechanism now competes with the S_N2 process.[18] However, selective removal of the ethoxycarbonyl group in a mixed benzyl ethyl malonate is observed (DMSO, H_2O, NaCl, 180°; 2-C_8)[82], which means that the benzyl group is not amenable to an S_N1-type cleavage, at least not under these conditions.

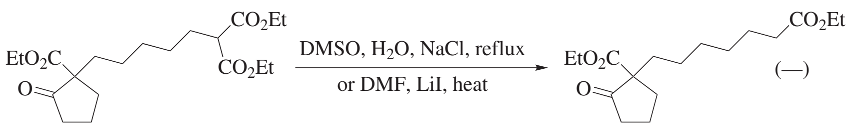
When both a geminal diester and a β-keto ester are present in one molecule, the latter may be dealkoxycarbonylated selectively, either in the presence (Eq. 30)[83] or absence (11B-C_{13-14})[84] of an inorganic salt. The latter reaction takes advantage of the fact that α,α-disubstituted malonates require the presence of an inorganic salt, whereas α-monosubstituted β-keto esters do not. Under more drastic conditions, both are dealkoxycarbonylated (Eq. 30;[83] 9B-C_{12}[85]). However, one paper reports a geminal diester reacting selectively in the presence of a β-keto ester under a number of different conditions (Eq. 31).[86] Reaction conditions that cause selective dealkoxycarbonylation of β-keto esters, but not of geminal diesters (4-dimethylaminopyridine, wet toluene, reflux),[87] are mentioned in the Comparison with Other Methods section.



18 **19**

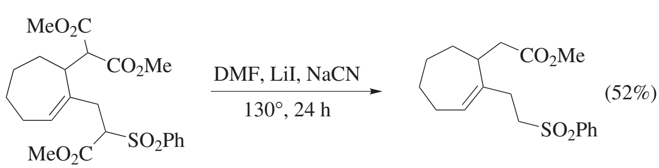
(Eq. 30)

Additive(s)	Temp (°)	Time (h)	Yield (%) 18	19
NaCl	150–160	2	83	0
LiI, py	165	13	0	72



(Eq. 31)

Selective dealkoxycarbonylation of an α-alkoxycarbonyl lactam in the presence of a geminal diester in refluxing DMF is shown in Eq. 79. Both a geminal diester and an α-sulfonyl ester are dealkoxycarbonylated in the only example where these two functional groups are present in one molecule (Eq. 32).[88] However, a rather extended reaction time is used and product samples after shorter times were not analyzed.



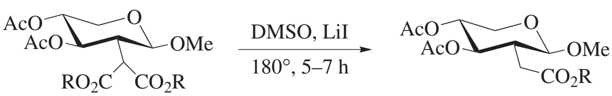
(Eq. 32)

SCOPE AND LIMITATIONS

In many equations in this section the preparation of the precursors is also given in order to illustrate the numerous different ways such systems can be generated.

Reaction Parameters

The Ester. Methyl and ethyl esters are by far the most widely used substrates for the Krapcho dealkoxycarbonylation. The former have the advantage of potentially increased reactivity and simpler NMR spectra. In the few examples where a direct comparison is possible, diisopropyl malonates give comparable or somewhat lower yields than the corresponding dimethyl malonates (Eq. 33).[89]



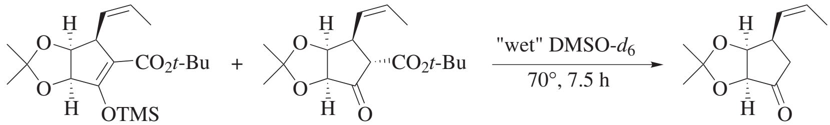
R	Yield (%)
Me	81
i-Pr	82

(Eq. 33)

Refluxing di-*tert*-butyl malonate in DMSO/water leads to rapid formation of *tert*-butyl acetate and *tert*-butanol.[18] No dealkoxycarbonylation of a substituted di-*tert*-butyl malonate was found in the literature. Attempted Krapcho reaction of a substituted mixed ethyl *tert*-butyl malonate met with failure (3-C_7).[90] However, examples of successful dealkoxycarbonylations of α-*tert*-butoxycarbonyl lactones (Eq. 34) and lactams (8C-C_{10}[94]) as well as numerous ones of β-keto *tert*-butyl esters have been reported. Some of these are carried out in the presence of an inorganic salt, but others are not. An example of the latter, which proceeds under remarkably mild conditions, is shown in Eq. 35.[95] In view of this result, addition of a salt would seem unnecessary in reactions of *tert*-butyl esters that proceed by the S_N1-type mechanism (Scheme 2). However, in a different system, addition of lithium chloride does increase the yield (Eq. 36),[18] indicating a partial shift to the $B_{AL}2$ mechanism. A few examples of the dealkoxycarbonylation of allylic esters have been published: a substituted digeranyl malonate in the patent literature (LiCl, HMPA, 130°, 85%; 2-C_{18})[96] and a β-keto allyl ester ($MgCl_2$•$6H_2O$, DMF, reflux, 91%; 11B-C_{10-13}).[97]

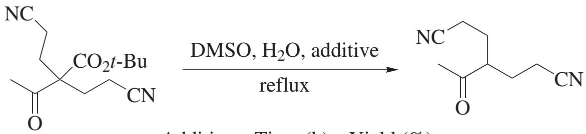
(Eq. 34)

R^1	R^2	Config.	Additive	Temp (°)	Time (h)	Yield (%)	er	Refs.
n-Bu	Me	(*S*)	NaCl	150	4	83	—	91
i-Bu	Et	(*S*)	LiCl	140	18	79	99.5:0.5	92
3-$MeOC_6H_4CH_2$	*t*-Bu	(*R*)	LiCl	140	17	65	96.0:4.0	93



60:40 (100%)

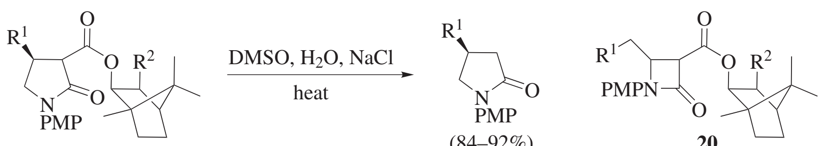
(Eq. 35)



(Eq. 36)

Additive	Time (h)	Yield (%)
—	3	60
LiCl	5	90

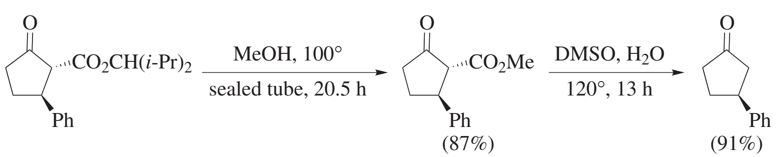
Activated esters involving chiral, non-racemic alcohols, used in preceding steps as chiral auxiliaries, have been submitted to the Krapcho dealkoxycarbonylation and this process can be very efficient even when very bulky alcohols are involved (Eq. 37;[98] 11A-C_{14}[99]). Perhaps the mechanism in this case involves S_N1 cleavage (Scheme 2) to form a non-classical carbocation. It is not clear whether the chiral auxiliary is recovered unchanged.[98] However, the β-lactams **20** give complex mixtures under the same conditions and in this case the chiral auxiliary is recovered unchanged. Dealkoxycarbonylations involving menthyl and phenylmenthyl esters are less efficient, with yields, when reported at all, that are fair to good at best (Eq. 104; 11A-C_7;[100] 11B-C_{10};[101,102] 16-C_{2-9}[103]). On occasion, bulky esters are converted into methyl esters by transesterification prior to dealkoxycarbonylation[104,105] (Eq. 38).[104]



20

R^1 = *n*-Bu, *c*-C_6H_{11}, Ph
R^2 = 1-naphthyl
PMP = 4-$MeOC_6H_4$

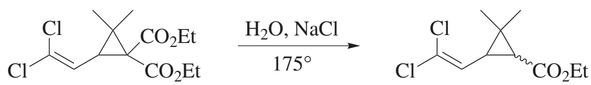
(Eq. 37)



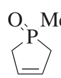
(Eq. 38)

Thus, even though there are examples of remarkable selectivity, there are many more instances where esters of different type and steric bulk are successfully dealkoxycarbonylated by the Krapcho method in many more instances.

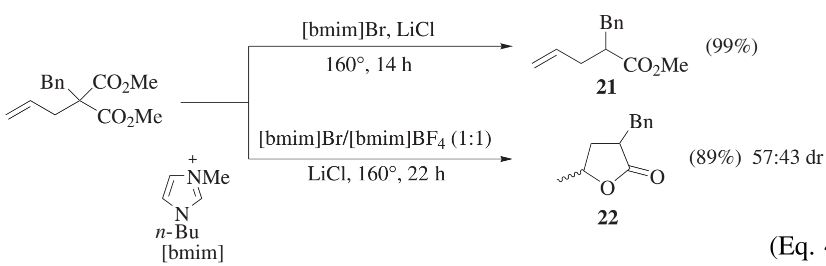
Solvents. Dimethyl sulfoxide (bp 189°) is still the most widely used solvent for Krapcho dealkoxycarbonylations. Because of its thermal instability, it was replaced in a large-scale synthesis by *N*-methylpyrrolidinone (NMP, bp 202°).[106,107] The higher-boiling di-*n*-butyl sulfoxide may be used if a volatile product with a boiling point similar to that of DMSO is distilled directly from the reaction mixture (Eq. 61).[108] Dimethylformamide is also widely used as solvent in these decarboxylation reactions. Dealkoxycarbonylation of β-keto ester **2** in Eq. 4 ($R^1 = R^2 =$ Me) with sodium cyanide proceeds 30-times faster in HMPA than in DMF[22] and the qualitative solvent effect on the rate of dealkoxycarbonylation of another β-keto ester with magnesium chloride is HMPA > DMSO > DMF.[109] However, HMPA is a suspected human carcinogen and it has been pointed out that it is often difficult to separate it from the product, whereas products can be selectively extracted from DMSO/water mixtures with a variety of solvents.[110] The cyclic urea *N*,*N*′-dimethylethyleneurea (DMEU; bp 224°) in combination with lithium iodide has been introduced as an alternative to HMPA,[111] and *N*,*N*′-dimethyl-*N*,*N*′-propyleneurea [DMPU; bp 146° (44 mm)], *N*,*N*-dimethylacetamide (bp 165°), and, in the patent literature, 1-oxo-1-methylphospholine and similar solvents[112,113] have also been used. The latter are claimed to give better yields (Eq. 39)[113] and, unlike DMSO, may be recovered from an aqueous mixture. An example is given in the Experimental Procedures section. However, use of this solvent in the dealkoxycarbonylation of an α-monosubstituted malonate gives no improved yields compared to the same reaction carried out in DMSO (2-C_{6-12}).[114]



(Eq. 39)

Solvent	Time (h)	Yield (%)
DMSO	9	15–20
	10	77

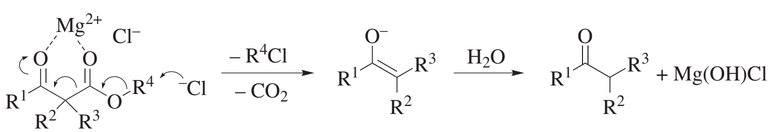
One report of an ionic liquid used as the reaction medium of a Krapcho dealkoxycarbonylation is known (Eq. 40).[115] The yields are comparable to those obtained with DMSO but the solvent is easily recovered. Ester **21** is formed when [bmim]Br is used, while lactone **22** is formed when a mixture of [bmim]Br and [bmim]BF_4 is used.



(Eq. 40)

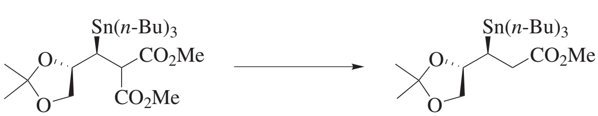
Salts. As mentioned previously, some substrates do not require the addition of inorganic salts for a successful Krapcho dealkoxycarbonylation. Thus diethyl phenylmalonate, 1-ethoxycarbonylcyclopentanone, and ethyl cyanoacetate undergo dealkoxycarbonylation in wet DMSO in the absence of a salt[116] at temperatures and with yields that are comparable to those where sodium chloride is added. Many α-monosubstituted malonates, however, either require, or benefit from, the addition of a salt. Thus in the dealkoxycarbonylation of dimethyl 2-(4-methylpentyl)malonate, LiCl, NaCl, KCl, NaBr, LiI, NaCN, $CaCl_2$, Na_3PO_4 and even Na_2CO_3 all give yields close to 100%, whereas with water alone the yield is only 10%.[20]

There appears to be no exception to the rule that dealkoxycarbonylations of α,α-disubstituted activated esters require the presence of a salt. The most widely applied salt in such cases is sodium chloride, but it is poorly soluble in the solvents used and lithium halides, with the exception of the fluoride,[15] are better choices. Sodium and potassium cyanide have also been used extensively, but they may also displace a halide present in the substrate (Eq. 57), cause ring-opening of a cyclopropane derivative (4A-C_5),[150] act as a base in an undesired reaction (Scheme 13), or cause the ester products to be hydrolyzed to the acids (Eq. 68). Lithium carbonate, a reaction product when lithium salts are used, is essentially inactive in the dealkoxycarbonylation of dimethyl α,α-diethylmalonate.[15] The group-IIa metal chlorides $CaCl_2{\bullet}2H_2O$ and $MgCl_2{\bullet}6H_2O$[109,110] are frequently used with β-keto esters, especially hindered ones (Eq. 86), and, less frequently, with geminal diesters and α-cyano esters. A mechanism involving initial formation of a magnesium chelate with the 1,3-dicarbonyl system has been proposed (Eq. 41).[110] Other metal chlorides, such as CuCl, $NiCl_2$, $ZnCl_2$, $MnCl_2$, or $SnCl_2$, are inactive. When malonates are dealkoxycarbonylated with $MgCl_2{\bullet}6H_2O$, cleavage of acetonide protecting groups followed by cyclization to form lactones has been observed (Scheme 14; 2-C_7).[173]



(Eq. 41)

Both metal (2-C_{10};[118] 2-C_9;[119] 3-C_{6-16}[120]) and tetraalkylammonium acetates[121] (Eq. 42;[122] Eq. 58[117]) often show enhanced reactivity as compared to other salts. Potassium trifluoroacetate has been used in one report (3-C_{10}).[123]

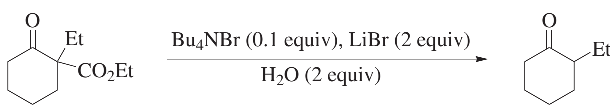


(Eq. 42)

Conditions	Yield (%)
DMSO, NaCl, 160°, 24 h	0
HMPA, $Me_4N^+AcO^-$, 100°, 1.5 h	53

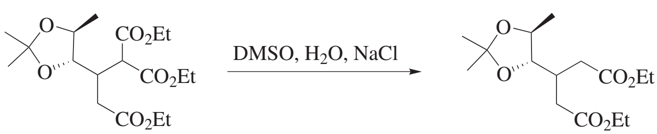
Other Additives. Addition of a small amount of a crown ether (12-c-4) increases the rate of dealkoxycarbonylation of a β-keto ester.[124,125] A phase-transfer catalyst [(*n*-Bu)$_4$NBr] increases the rate of dealkoxycarbonylation of an α-cyano ester with NaCl, but not with the more soluble LiCl.[125a] Alkylation of the intermediate enolate by the alkyl halide formed in dealkoxycarbonylations involving salts is avoided by the addition of an acid (Scheme 6), 4-aminothiophenol (Eq. 14), or ethyl mercaptan.[110] The latter additive also prevents air oxidation of the intermediate enolate.[110] With vinylogous β-keto esters, the bulkier *t*-BuSH or *t*-C_7H_{15}SH is recommended to preclude Michael addition of the mercaptan to the activated double bond (Eq. 111). Addition of traces of di-*tert*-butylhydroquinone is beneficial in the dealkoxycarbonylation of an α-nitro ester (Eq. 103).[126]

Microwave Irradiation.[127,128] A number of Krapcho dealkoxycarbonylations have been carried out using microwave irradiation (Mw). The reaction shown in Eq. 43 is carried out in an open vessel without a solvent in the presence of a phase-transfer agent.[129] The control experiments show clearly that microwave irradiation not only provides the heat source but that it also intrinsically speeds up the reaction. This has been attributed to a reduction of the activation energy for the polar transition structure in the $B_{AL}2$ mechanism.[130] The reaction shown in Eq. 44,[131] carried out in a solvent, is an example where the conventional Krapcho reaction fails.



(Eq. 43)

Temp (°)	Time	Yield (%)
Mw, 160	15 min	94
160	15 min	0
160	60 min	22
160	3 h	60



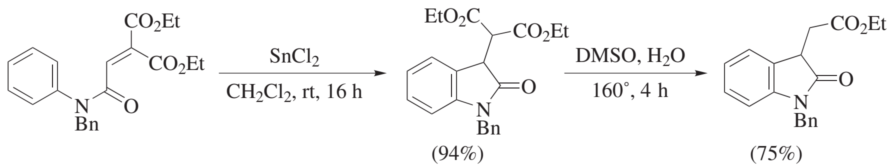
(Eq. 44)

Conditions	Yield (%)
160°, 3 h	0
Mw (800 W), 15 min	58

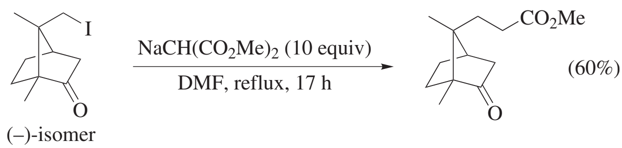
Microwave-assisted dealkoxycarbonylations in sealed tubes are limited to very small amounts because the carbon dioxide evolved may cause explosions in larger runs. However, the standard solvents used in the Krapcho dealkoxycarbonylation are high boiling. Therefore reactions can be done in open vessels and the temperature can be kept below the boiling by controlling the power output. Whether the solvent-free method is generally applicable and can be used on a large scale remains to be determined.

Geminal Diesters

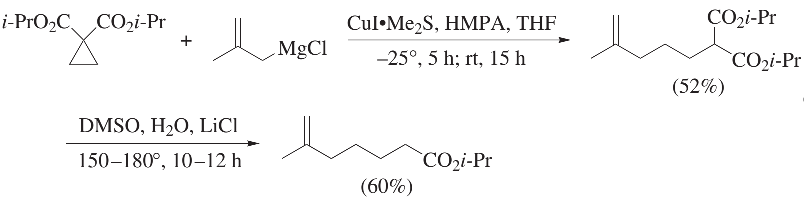
α-Monosubstituted Malonates (Table 2). As mentioned previously, only a few monosubstituted malonates, such as diethyl phenylmalonate, diethyl benzylmalonate, and diethyl acetamidomalonate, are dealkoxycarbonylated in high-boiling polar solvents in the presence of water only. Another example is shown in Eq. 45.[132] Most others require the addition of a salt. In the one-pot procedure shown in Eq. 46,[133] the sodium iodide formed in the alkylation step fulfills this role. The iodine in the substrate may be substituted by a quaternary ammonium salt in such one-pot procedures (2-C_{15}).[134] An example where the substrate is generated by reaction of a Grignard reagent with a cyclopropane-1,1-diester is shown in Eq. 47.[135] Michael addition to a putative aza orthoquinodimethane intermediate is used to prepare the substrate in the reaction shown in Eq. 48.[136]



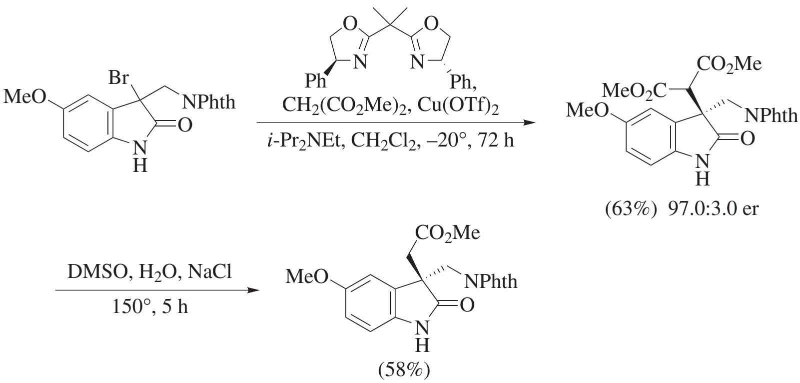
(Eq. 45)



(Eq. 46)

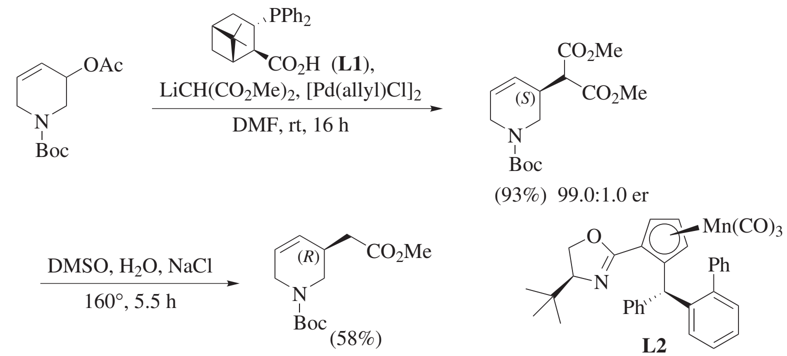


(Eq. 47)

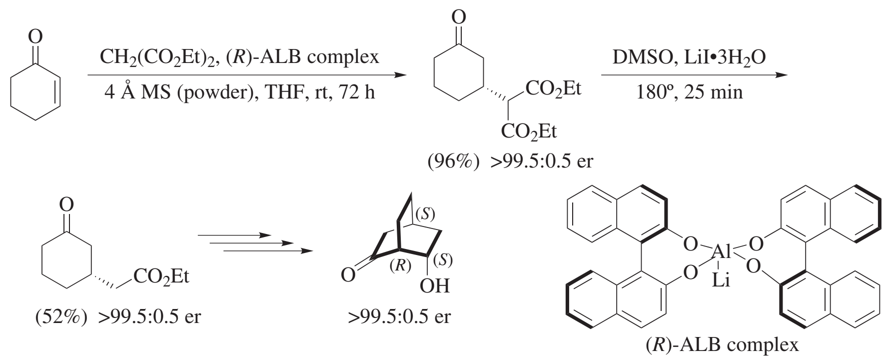


(Eq. 48)

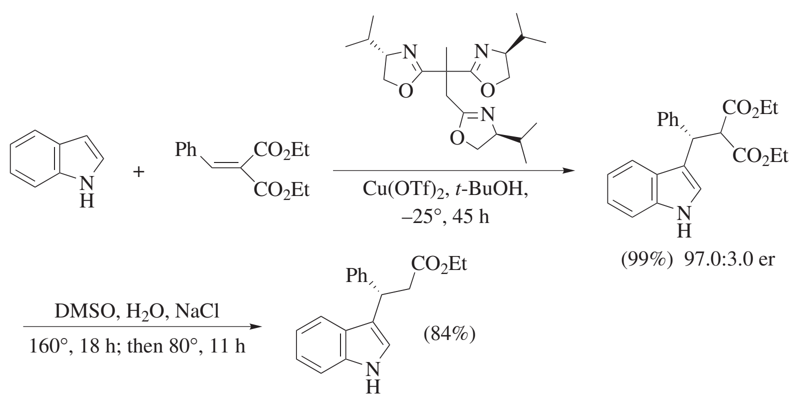
Palladium-catalyzed alkylation of the allylic acetate in Eq. 49, using ligand **L1**, gives the (*S*)-malonate substrate for a Krapcho dealkoxycarbonylation, whereas with ligand **L2** the (*R*)-isomer is formed.[137] A synthesis of (1*R*,4*S*,6*S*)-6-hydroxybicyclo[2.2.2]octan-2-one involves asymmetric addition of diethyl malonate to cyclohex-2-en-1-one and subsequent dealkoxycarbonylation followed by three additional steps (Scheme 10).[73,138] Asymmetric Friedel−Crafts reaction of indole provides the substrate for the dealkoxycarbonylation in Eq. 50.[139]



(Eq. 49)

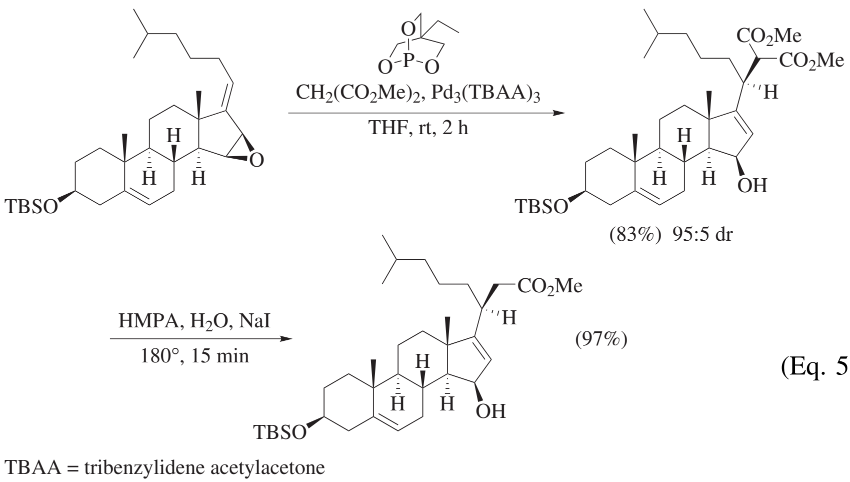


Scheme 10



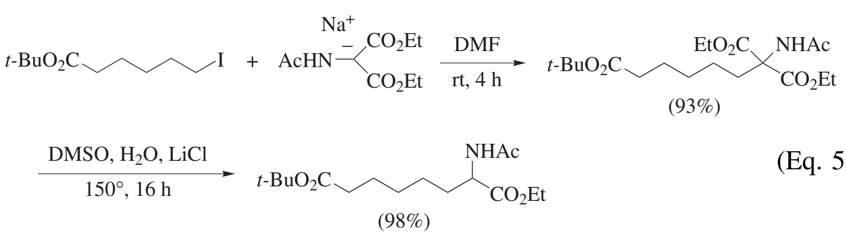
(Eq. 50)

Palladium-catalyzed addition of dimethyl malonate to a steroid 1,3-diene monoepoxide is a key step in the synthesis shown in Eq. 51.[140]

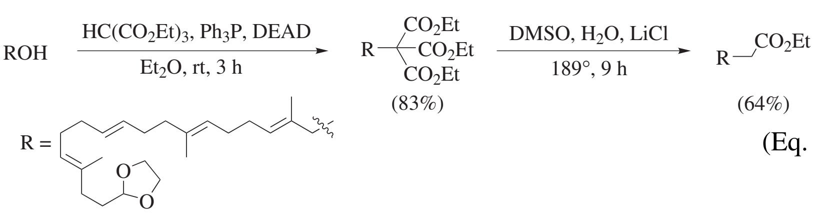


(Eq. 51)

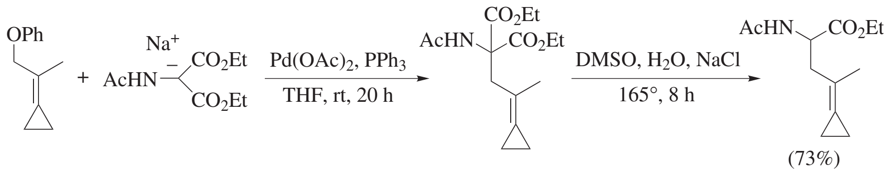
α,α-Disubstituted Malonates (Table 3). These substrates may be prepared from halides (Eq. 52),[141] from alcohols by Mitsunobu coupling (Eq. 53),[142] or from allylic systems (Eq. 54).[143] Of note in Eq. 53 is that two of the three alkoxycarbonyl groups of the triester are removed in the dealkoxycarbonylation. Other examples of this process are known (3-C_{10});[144] however, the malonate may be obtained by lowering the temperature (Eq. 55).[145]



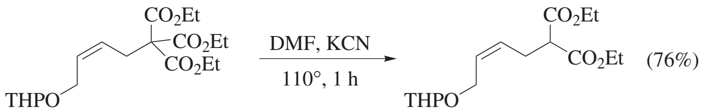
(Eq. 52)



(Eq. 53)

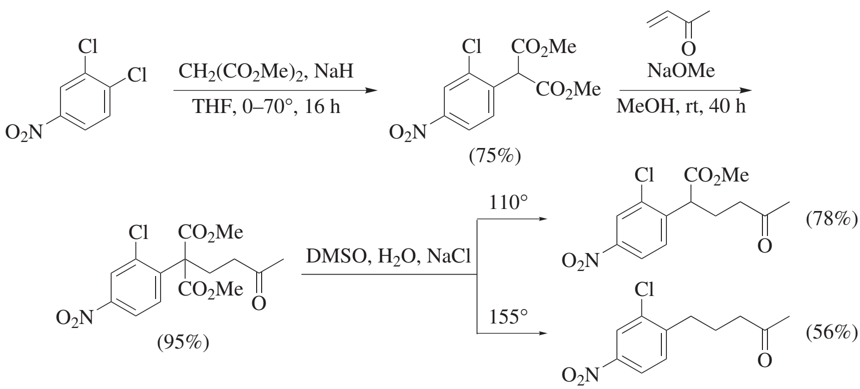


(Eq. 54)

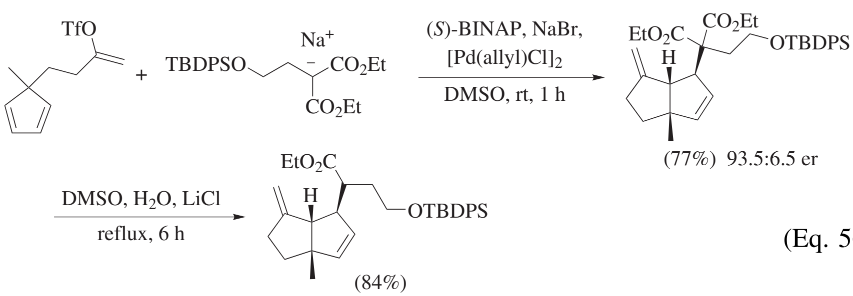


(Eq. 55)

Activated aryl halides may also be used for preparing α,α-disubstituted malonates (Scheme 11).[146] In this reaction one or both esters may be eliminated in the subsequent Krapcho dealkoxycarbonylation depending on the temperature used. The primary product is a phenylogous nitro ester and thus subject to further reaction. Reactions of this type are discussed in the section on Vinylogous and Phenylogous Activated Esters. Loss of both ester groups is also observed in an iron complex of diethyl phenylmalonate (2-C_9)[147] so that this phenomenon may be general for arylmalonic esters containing strongly electron-withdrawing substituents. A tandem intramolecular Heck reaction/anion-trapping is used to prepare the substrate in Eq. 56.[148]

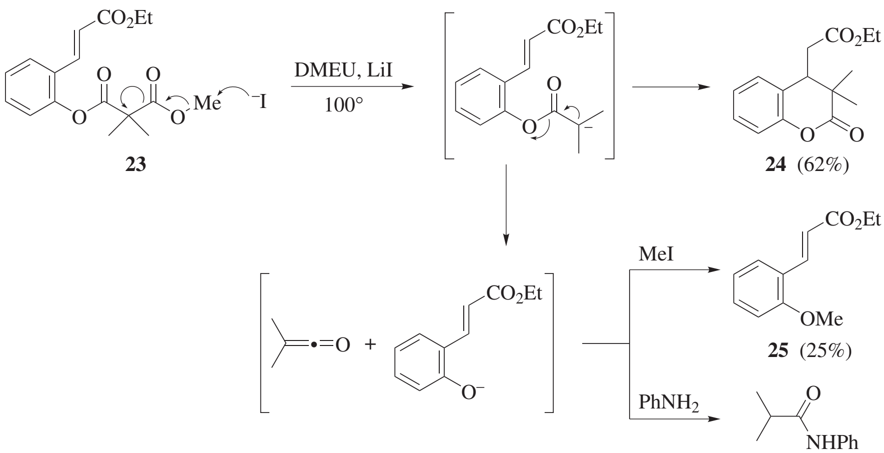


Scheme 11

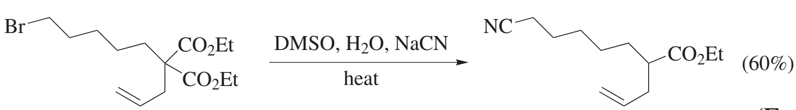


(Eq. 56)

Heating the phenyl malonate **23** with lithium iodide in N,N'-dimethyl-N,N'-ethylene urea gives the methyl ether **25** and dimethylketene, which can be trapped by aniline (Scheme 12).[111] Phenoxide as a good leaving group facilitates the extrusion of the ketene. Whether phenyl malonates in general are susceptible to this side reaction remains to be determined. No ketene formation is observed in the dealkoxycarbonylation of the corresponding anilide, reflecting the much poorer leaving property of anilide anion.[111] The main product **24** results from an intramolecular Michael addition of the initially formed enolate to the α,β-unsaturated ester function, a reaction that is discussed further in the section entitled Trapping of the Intermediate Enolates by Electrophiles Other Than a Proton. A bromide may be displaced simultaneously with dealkoxycarbonylation when cyanide is used as the salt additive (Eq. 57).[149]

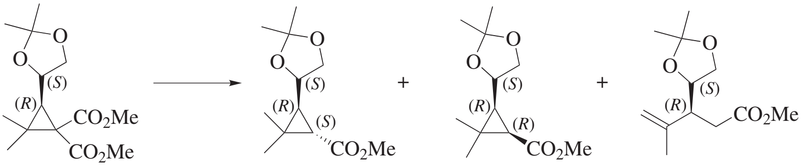


Scheme 12



(Eq. 57)

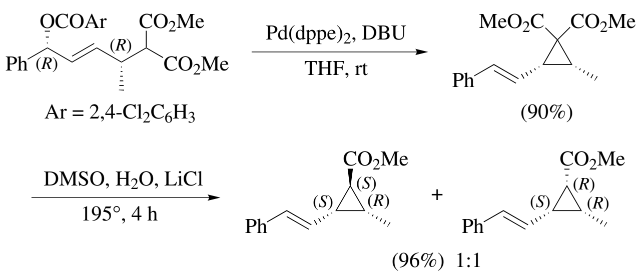
Cyclic Geminal Diesters. *Three-Membered Cyclic Geminal Diesters (Table 4A).* Treatment of diethyl cyclopropane-1,1-dicarboxylate with a substoichiometric amount of sodium cyanide in HMPA at 150° results in formation of the ring-opened diethyl 2-cyanoethylmalonate (4A-C_5).[150] Partial cleavage of a cyclopropane ring by either sodium cyanide or sodium chloride is also observed in the reaction of Eq. 58.[117] Use of tetramethylammonium acetate not only prevents ring opening, but also lowers the reaction temperature and increases the yield.



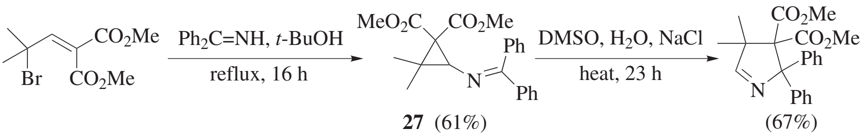
(Eq. 58)

Conditions	Yield (%) *trans*	*cis*	**26**
DMSO, H_2O, NaCl, 160°, 6 h	20	15	38
DMF, H_2O, NaCN, 120°, 48 h	44	30	14
DMPU, $Me_4N^+AcO^-$, 95°, 4 h	50	27	0

Dealkoxycarbonylation of 2-vinylcyclopropane-1,1-dicarboxylate with sodium cyanide in refluxing DMSO fails,[151] but cyanide succeeds with other substituted cyclopropane-1,1-diesters. As mentioned in the Diastereoselectivity section, cyclopropane-1,1-diesters with other resident stereogenic centers give mixtures of *cis*- and *trans*-esters in which the latter often predominate or are formed exclusively (Eq. 5), although the reverse is true in a rare case (Eq. 6). 1-Oxo-1-methylphospholine is claimed to be a better solvent than DMSO for the dealkoxycarbonylation of cyclopropane-1,1-diesters (Eq. 39). Cyclopropane-1,1-diesters are accessible by a variety of methods. One, involving palladium-catalyzed cyclization of an allylic benzoate, is shown in Eq. 59.[152] Diester **27** undergoes a vinylcyclopropane-to-cyclopentene-like rearrangement and the product is not dealkoxycarbonylated (Eq. 60),[153] probably for steric reasons.



(Eq. 59)



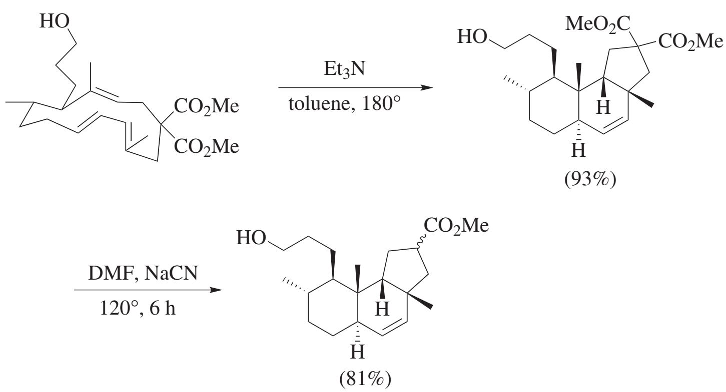
(Eq. 60)

Four-Membered Cyclic Geminal Diesters (Table 4B). Most of the reported examples involve β-lactams; the nitrogen in these systems must be protected (4B-C_5).[154] Diastereochemical issues are discussed in the section on Selectivity (Eqs. 7 and 8). In contrast to its lower homolog, diethyl cyclobutane-1,1-dicarboxylate is readily dealkoxycarbonylated with cyanide (Eq. 61). By using the higher-boiling dibutylsulfoxide (bp 250°), ethyl cyclobutanecarboxylate (bp 159°) distills directly from the reaction mixture. The 2-(4′-bromophenyl) derivative gives exclusively the *trans*-product, presumably under thermodynamic control, whereas the 3-benzyl ether gives a mixture of both isomers (Eq. 61).

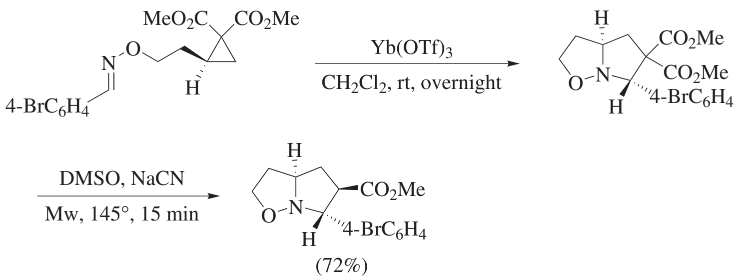
(Eq. 61)

R^1	R^2	Conditions	Yield (%)	*cis*/*trans*	Refs.
H	H	DMSO, NaCN, 160°, 4 h	75	—	108
H	H	$(n\text{-Bu})_2SO$, NaCN, 160°, 4 h	65	—	108
H	4-BrC_6H_4	DMSO, H_2O, LiCl, reflux, 4 h	72	0:100	155
BnO	H	DMSO, H_2O, NaCl, 210°, 48 h	88	56:43	156

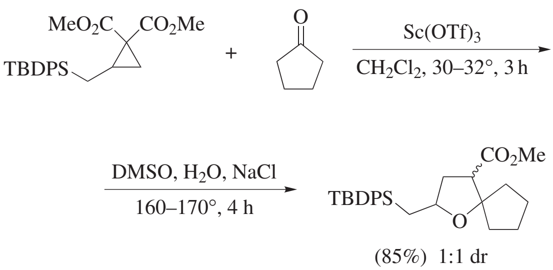
Five- and Higher-Membered Cyclic Geminal Diesters (Tables 4C–4E). These substrates, in most cases, are readily dealkoxycarbonylated in good to excellent yields. Examples of 5-membered cyclic substrates are illustrated in Eqs. 62,[157] 63,[158] and 64.[159]



(Eq. 62)

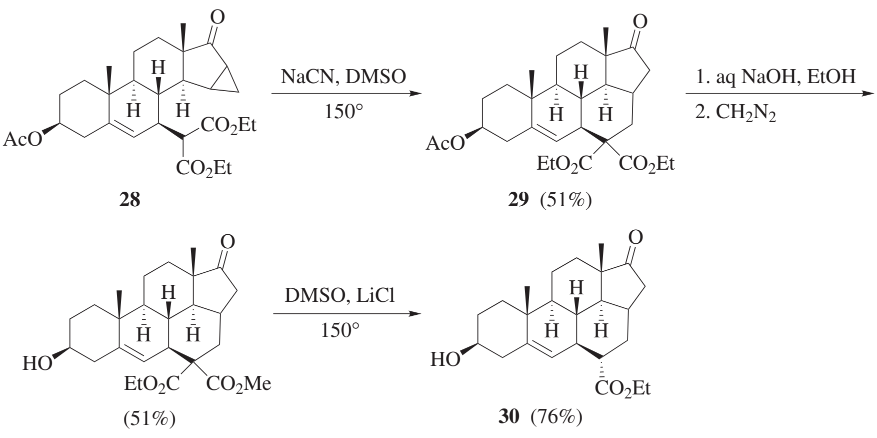


(Eq. 63)



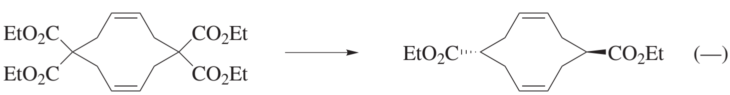
(Eq. 64)

An interesting case involving the six-membered steroid **28** is shown in Scheme 13.[160] Attempted dealkoxycarbonylation with sodium cyanide in DMSO leads to the cyclized product **29** instead, with the cyanide acting as a base to deprotonate the malonate. The expected monoester is obtained when lithium chloride is used. Diester **29** is resistant to dealkoxycarbonylation with either sodium cyanide or sodium chloride in refluxing DMF. However, the mixed methyl ethyl ester, prepared by partial hydrolysis and re-esterification, is selectively transformed into a single isomer of the ethyl ester **30**.



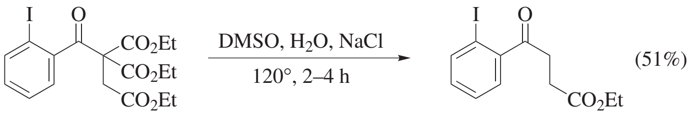
Scheme 13

Double dealkoxycarbonylation of the ten-membered tetraester shown in Eq. 65 is reported to give the *trans*-diester but experimental details were not given.[161]

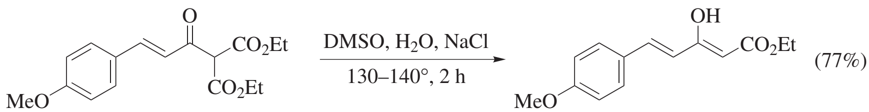


(Eq. 65)

α-Acyl Malonates (Table 5). Only a few examples of the Krapcho dealkoxycarbonylation of this substrate type were found in the literature. The products are β-keto esters which, as reactive substrates themselves, can give ketones in a second step (Eq. 66).[162] Reactions can stop at the β-keto ester stage, in the case of Eq. 67[163] perhaps because the extended conjugation makes the product less prone to further dealkoxycarbonylation. The best, and environmentally most benign, method for converting α-acyl malonates into β-keto esters is to heat them with water (Table 5).

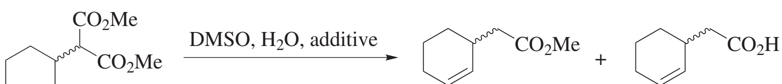


(Eq. 66)



(Eq. 67)

Same-Pot Subsequent Reactions of the Ester Products. On occasion, acids are obtained instead of, or in addition to, the esters in Krapcho dealkoxycarbonylations. This seems to happen mostly, though not exclusively, with cyanide as the salt additive, and extended reaction times. For example, overnight reaction of geminal diester **31** with NaCN in DMSO/H_2O exclusively affords carboxylic acid **33**, whereas the same reaction performed with LiI in 1.5 hours exclusively affords methyl ester **32** (Eq. 68). Thus if the isolation procedure includes a base wash, it is advisable to check it for any carboxylic acid that may have been formed. Diethyl 7,7-norcaranedicarboxylate gives the diacid in 65% yield with potassium cyanide in refluxing DMF.[167]

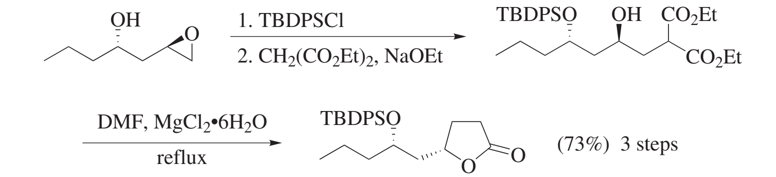


31 **32** **33**

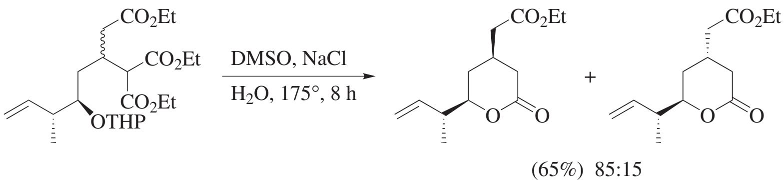
Config.	er	Additive	Temp (°)	Time (h)	Yield (%) 32	Yield (%) 33	er	Refs.
(*S*)	—	NaCN (2 equiv)	160	—	"good"	0	—	164
(*S*)	97.0:3.0	NaCN (2.3 equiv)	189	overnight	0	94	91.0:9.0	164
(*R,S*)	—	NaCl	189	1.5	94	0	—	165
(*R,S*)	—	LiI	180	1.5	85	0	—	166

(Eq. 68)

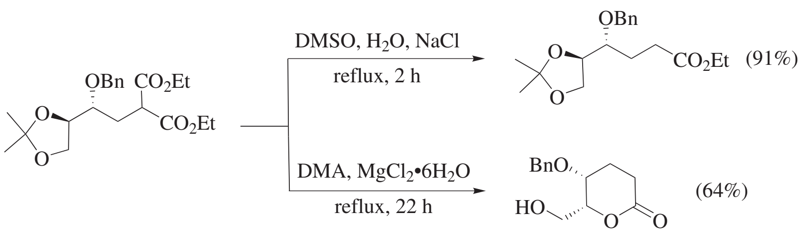
The presence of a free hydroxy group at the appropriate distance may lead to lactone formation during or after dealkoxycarbonylation (Eq. 69;[168] 4D-C_{21}[169]). Lactonization does not take place when the product would be a *trans*-fused bicyclo[3.3.0] (2-C_8)[170] or a bicyclo[4.2.1] system (2-C_9).[171] Tetrahydropyranyl ethers are normally not cleaved during Krapcho dealkoxycarbonylations but an exception is shown in Eq. 70, where subsequent cyclization leads to a lactone.[172] A similar sequence involving cleavage of an acetonide protecting group by magnesium chloride hexahydrate is shown in Scheme 14.[173] Use of sodium chloride in this dealkoxycarbonylation gives the expected ketal ester. Cleavage of a TMS group followed by lactone formation has been observed (Eq. 129). The presence of an enolizable keto group may also lead to lactone formation (Eq. 71).[174] Intramolecular addition of a carboxy group to a double bond to form a lactone under the influence of an ionic liquid is shown in Eq. 40.



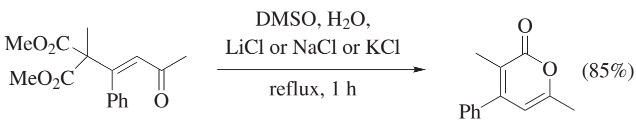
(Eq. 69)



(Eq. 70)

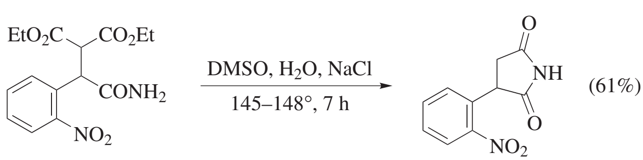


Scheme 14



(Eq. 71)

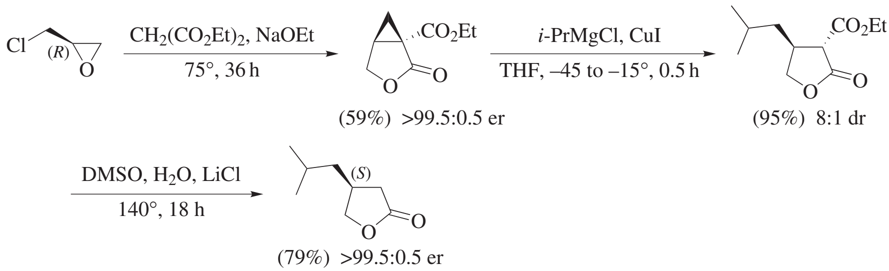
In a similar vein, lactams ($2\text{-}C_{11}$)[175] or imides (Eq. 72)[176] may be formed when amino or amido groups, respectively, are present at the appropriate distance.



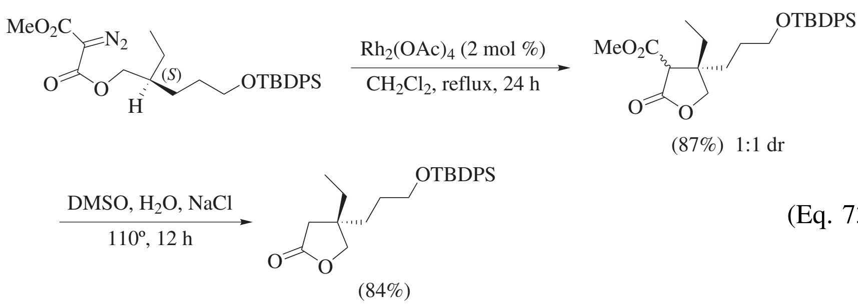
(Eq. 72)

α-Alkoxycarbonyl Lactones

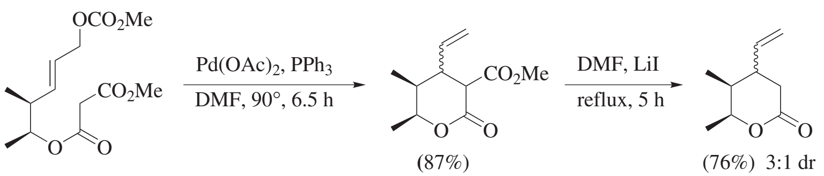
Dealkoxycarbonylation of α-alkoxycarbonyl lactones, listed in Tables 6A–6C, gives lactones in most cases. Examples are shown in Scheme 15,[92] and Eqs. 73,[177] 74,[178] and 75.[179]



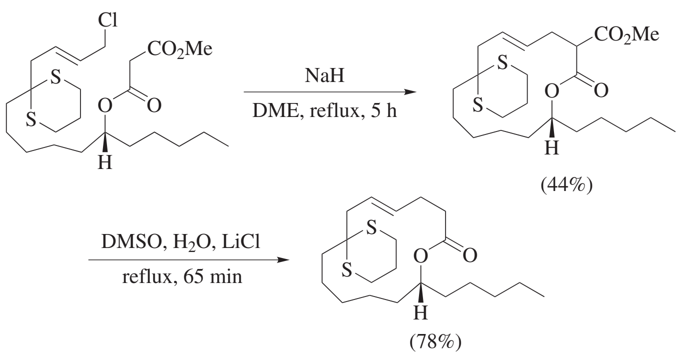
Scheme 15



(Eq. 73)

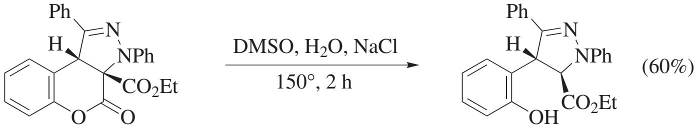


(Eq. 74)

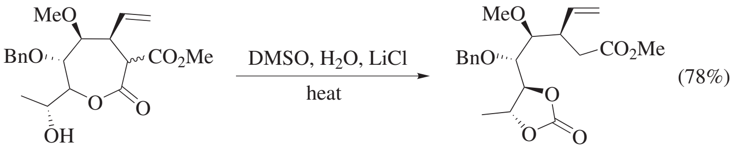


(Eq. 75)

The reactions of Eqs. 76[180] and 77[181] were reported without comment as to their mechanisms, but presumably involve initial attack of water on the lactone carbonyl group.



(Eq. 76)



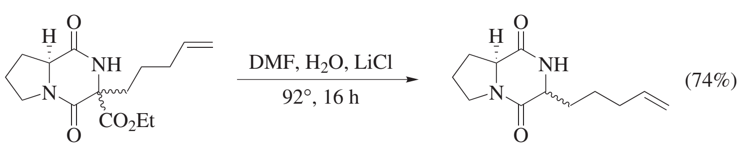
(Eq. 77)

α-Alkoxycarbonyl Amides

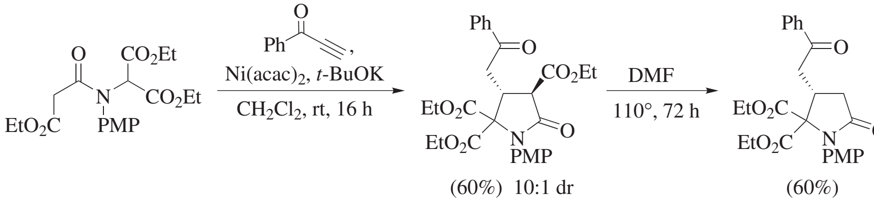
No Krapcho dealkoxycarbonylation of an α-alkoxycarbonyl amide was found in the literature. The two examples in Table 7 involve heating with water and refluxing in 2,4-lutidine, respectively. The latter type of reaction is discussed in Comparison with Other Methods. However, based on the results with α-alkoxycarbonyl lactams (Tables 8A–8D), α-alkoxycarbonyl amides, even *N*-unsubstituted ones, are expected to undergo normal Krapcho dealkoxycarbonylation.

α-Alkoxycarbonyl Lactams

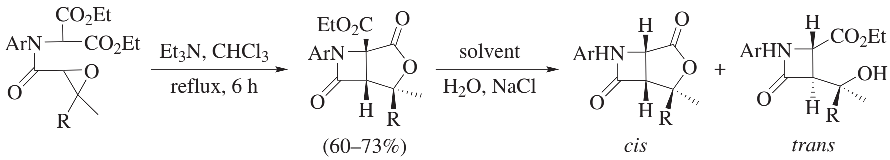
The examples listed in Tables 8A–8D show that both *N*-unsubstituted (Eq. 78)[182] and *N*-substituted (Eq. 79)[183] α-alkoxycarbonyl lactams undergo normal dealkoxycarbonylation under a variety of conditions. The latter, a general synthesis of pyroglutamic acid derivatives, involves a double Michael addition as the key step. Of note is that heating under reflux in DMF, without water or a salt, selectively removes the lactam α-ester while leaving the geminal diester intact. Dealkoxycarbonylation of α-alkoxycarbonyl lactams bearing very bulky ester groups is shown in Eq. 37. The lactone ring in the α-alkoxycarbonyl β-lactam shown in Eq. 80 partially or completely opens and the product epimerizes to the *trans*-isomer when the *N*-4-methoxyphenyl derivatives are used.[184] The normal product is obtained with the *N*-4-tolyl analog. No rationalization of this substituent (or solvent) effect has been advanced.



(Eq. 78)



(Eq. 79)

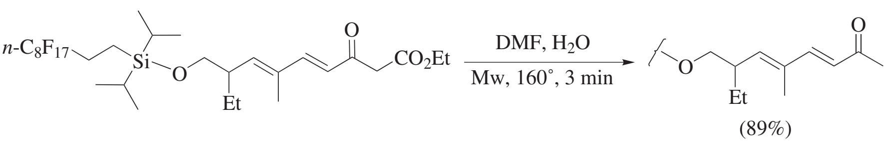


Ar	R	Solvent	Temp (°)	Time (h)	Yield (%) *cis*	Yield (%) *trans*
4-$MeOC_6H_4$	H	DMF	153	8	0	70
4-$MeOC_6H_4$	Me	DMF	153	12	40	29
4-MeC_6H_4	Me	DMSO	189	4	79	0

(Eq. 80)

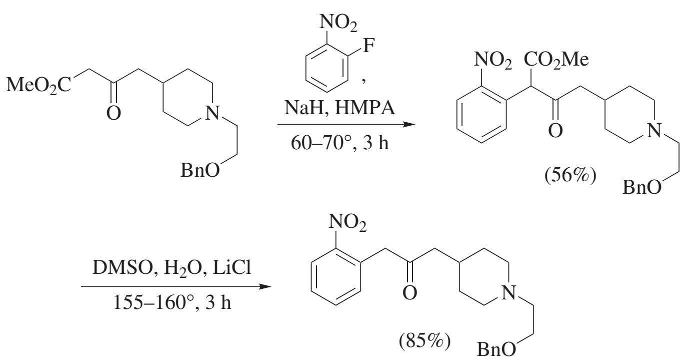
β-Keto Esters

α-Unsubstituted Acyclic β-Keto Esters. These substrates upon dealkoxycarbonylation give methyl ketones. Among the various methods that have been used (Table 9A), the Krapcho dealkoxycarbonylation is in the minority. Reactions have been carried out both with and without addition of a salt. An example of the latter is shown in Eq. 81.[17]

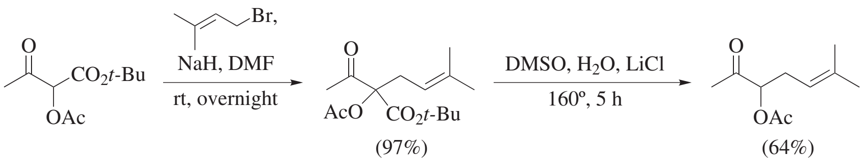


(Eq. 81)

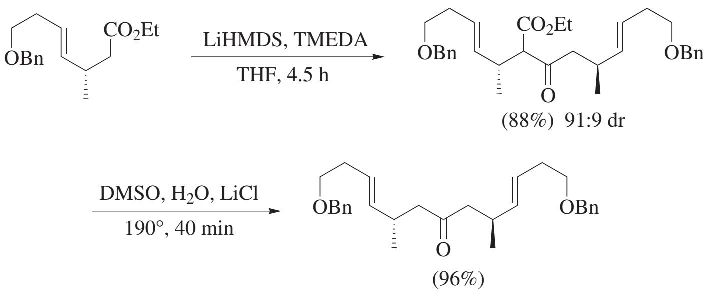
α-Mono- and α,α-Disubstituted Acyclic β-Keto Esters (Tables 9B and 9C). Dealkoxycarbonylation of these substrates is a versatile method for the preparation of a wide variety of acyclic ketones. β-Keto *tert*-butyl esters have been dealkoxycarbonylated both with and without a salt, whereas all other types of esters require the addition of a salt. The substrates are mostly prepared by modification of less complex β-keto esters (Eqs. 82[185] and 83[186]). Of note in the latter case is that the acetoxy group is not eliminated. In Eq. 84, the substrate derives from a Claisen self-condensation.[187]



(Eq. 82)

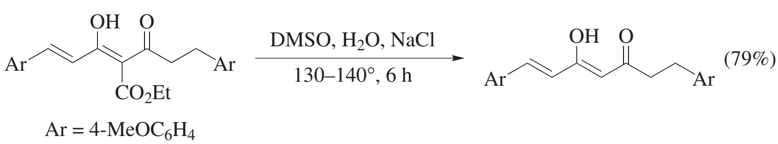


(Eq. 83)



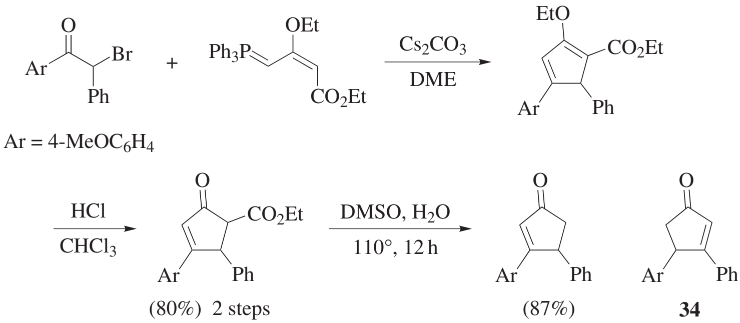
(Eq. 84)

α-Acyl β-Keto Esters (Table 10). 1,3-Diketones are formed in the dealkoxycarbonylation of α-acyl β-keto esters. Although the Krapcho method has been used for this transformation (Eq. 85),[163] simple heating with water seems to work just as well.



(Eq. 85)

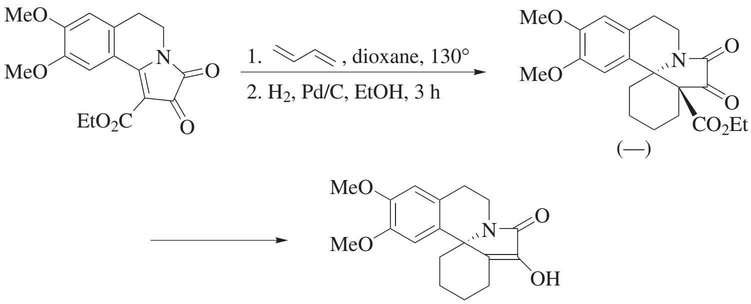
Cyclic β-Keto Esters (Tables 11A–11D). A large number of cyclic ketones have been prepared by Krapcho dealkoxycarbonylation of cyclic β-keto esters. A selection of examples follows. The substrate shown in Scheme 16 is prepared by an intramolecular Wittig reaction as the key step.[188] Dealkoxycarbonylation



34

Scheme 16

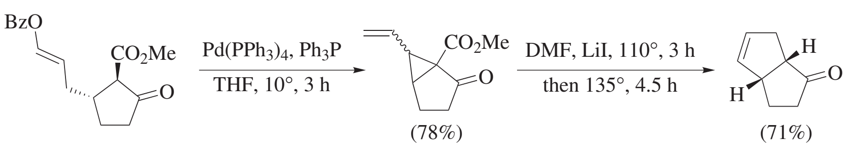
at 110° gives the desired product in high yield; when the temperature is raised to 140°, partial isomerization to enone **34** takes place. Equation 86[110] illustrates the dealkoxycarbonylation of a hindered β-keto ester where use of magnesium chloride lowers the reaction temperature and gives higher yields in a shorter time. The ethyl mercaptan is added to prevent air oxidation of the intermediate enolate and to prevent its alkylation by the ethyl chloride formed.



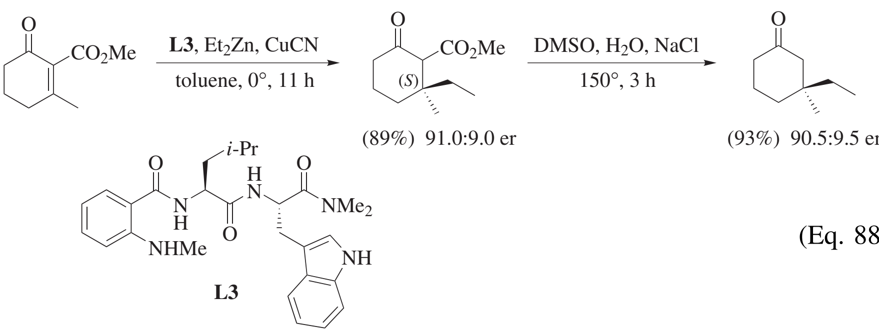
(Eq. 86)

Conditions	Yield (%)
DMSO, H_2O, NaCl, 170°, 24 h	27
DMSO, $MgCl_2$•$6H_2O$, EtSH, sealed tube, 155–160°, 6 h	63
HMPA, $MgCl_2$, Ar, 150–155°, 2 h	73
DMSO, $CaCl_2$•$2H_2O$, EtSH, 150°, 5 h	43

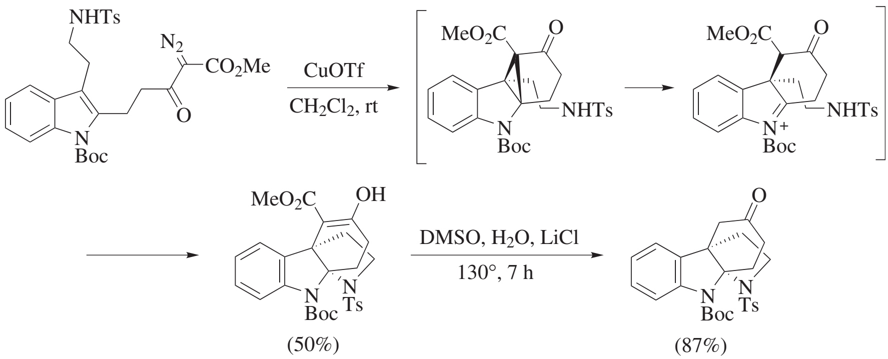
A vinylcyclopropane-to-cyclopentene rearrangement and dealkoxycarbonylation occur simultaneously in the reaction of Eq. 87.[189] An asymmetric Michael addition generates the substrate in Eq. 88.[190] The polycyclic ketone in Scheme 17 is formed by a one-pot cyclopropanation, ring-opening, and ring-closure sequence.[191]



(Eq. 87)

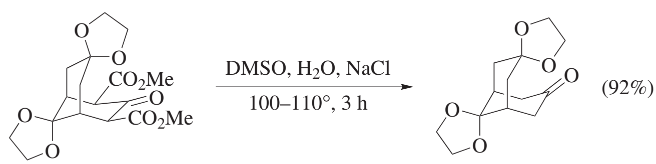


(Eq. 88)

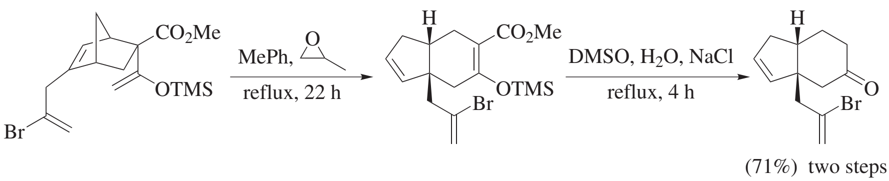


Scheme 17

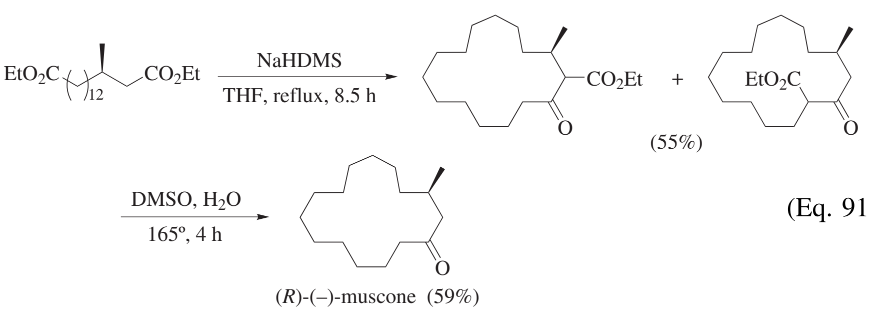
Two ester groups are efficiently removed in the substrate shown in Eq. 89.[192] Silyl enol ethers of β-keto esters may be used directly in the Krapcho dealkoxycarbonylation (Eq. 90). The product is a key intermediate in the synthesis of gibberellic acid.[193] Dieckmann cyclization provides the substrates for a synthesis of (*R*)-(−)-muscone (Eq. 91).[194]



(Eq. 89)

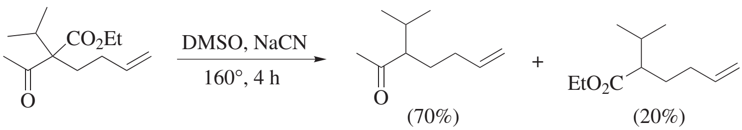


(Eq. 90)

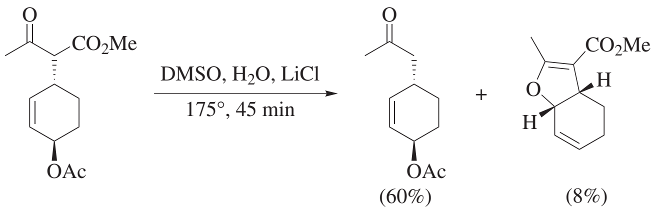


(Eq. 91)

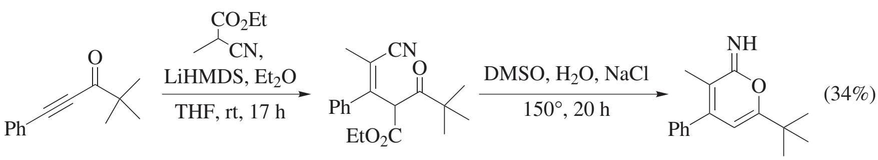
Side Reactions and Same-Pot Subsequent Reactions of the Keto Products. Reverse Michael cleavage followed by dealkoxycarbonylation occurs on rare occasions (9B-C_{14}).[195] Similarly, acid cleavage of a β-keto ester (hydrodeacylation) under Krapcho conditions appears to have been reported only once (9B-C_{13}).[196] There is one example where acyl cleavage competes with dealkoxycarbonylation (Eq. 92).[197] Addition of the oxygen of the intermediate enolate to an allylic acetate (Eq. 93)[198] and a cyano group (Eq. 94)[199] has been observed, as has formation of a lactone by condensation with a carboxy group (Eq. 95).[200]



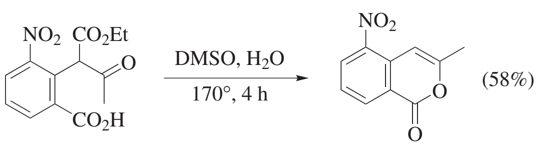
(Eq. 92)



(Eq. 93)

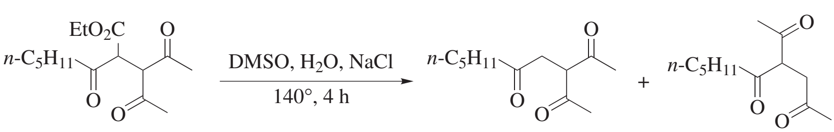


(Eq. 94)



(Eq. 95)

Dealkoxycarbonylation of triketo ester **35** gives the expected product **36** and its 1,2-acyl migration product **37** (Eq. 96).[201] This rearrangement, whose mechanism has not been established, is also observed with similar triketones. It is purely thermal and does not require the presence of either water or sodium chloride.

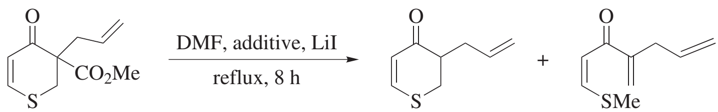


35 **36** **37**

36 + **37** (—), **36**/**37** = 1:1

(Eq. 96)

Dealkoxycarbonylation of the thiopyrane **38** gives mostly the elimination product **40** via a methylsulfonium intermediate when anhydrous conditions are used (Eq. 97).[125] Addition of water suppresses the elimination reaction by more efficient protonation of the intermediate enolate, and provides mainly the desired product **39**.

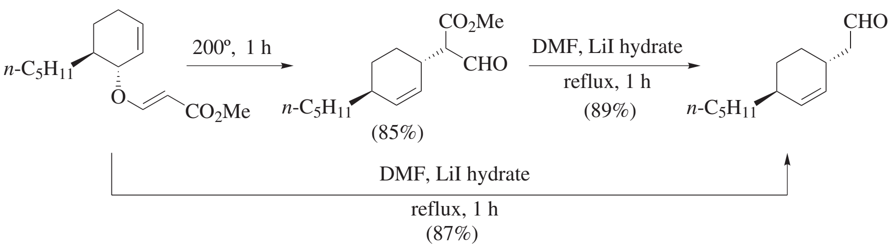


38 **39** **40** (Eq. 97)

	Yield (%)	
Additive	**39**	**40**
—	5	59
H_2O	66	9

α-Formyl Esters (Table 12)

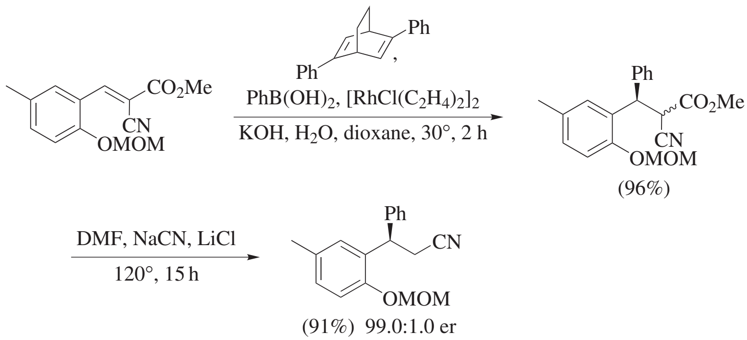
The only α-formyl ester subjected to a Krapcho dealkoxycarbonylation is prepared by a Claisen rearrangement. Both reactions may be carried out in one step (Scheme 18).[202]



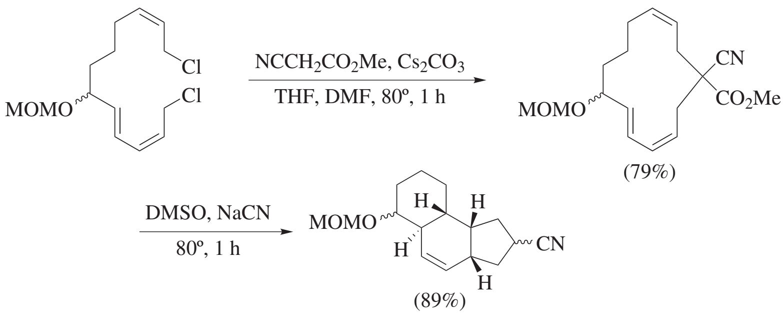
Scheme 18

α-Cyano Esters

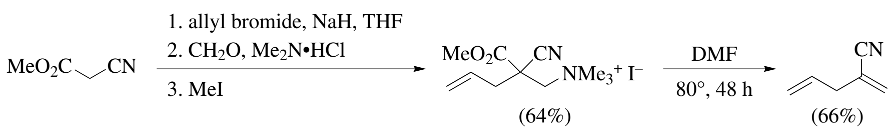
A large number of nitriles have been prepared in mostly good to excellent yields by Krapcho dealkoxycarbonylation of α-cyano esters (Tables 13A and 13B). The substrates are usually prepared from cyanoacetic esters by Michael addition (Eq. 98)[203] or alkylation (Eq. 99).[204] The conditions used for the dealkoxycarbonylation in the latter case effect an intramolecular Diels–Alder reaction as well. α,β-Unsaturated nitriles are formed from substrates that contain a neighboring trimethylammonium group (Eq. 100),[205] where the intermediate enolate undergoes a Hofmann elimination. No salt needs to be added since the iodide of the quaternary ammonium salt serves in this capacity. Three steps are carried out in one pot in the reaction shown in Scheme 19.[206] Extensive optimization of the reaction shown in Eq. 101 (see Table 13B-C_{11})[125a] determined that the rate of dealkoxycarbonylation with LiCl as the catalyst increases in the order of solvents used: H_2O (no reaction) < DMSO < DMF < NMP. Moreover, LiCl is a better catalyst than NaCl and addition of a phase-transfer catalyst increases the rate of the sodium chloride catalyzed reaction but has no effect with the more soluble LiCl. The dimethyl ester reacts substantially faster than the diethyl ester.



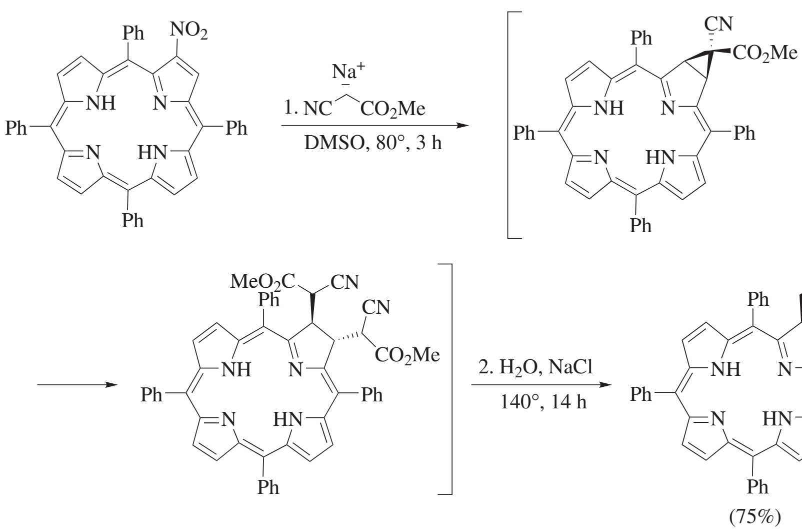
(Eq. 98)



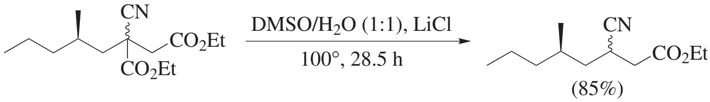
(Eq. 99)



(Eq. 100)

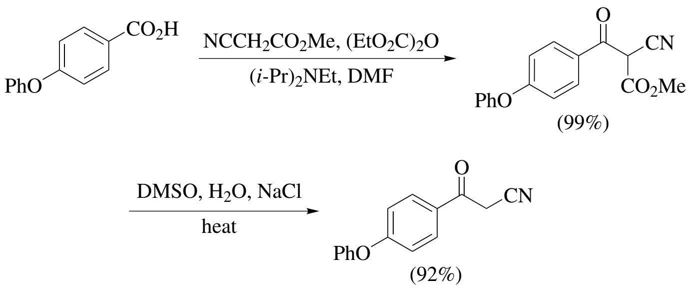


Scheme 19



(Eq. 101)

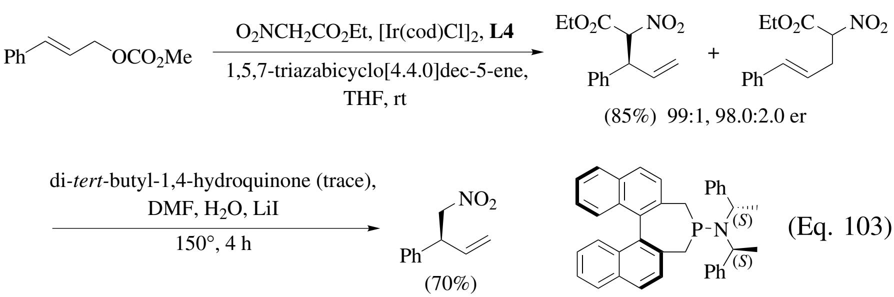
β-Keto nitriles are obtained by dealkoxycarbonylation of α-acyl α-cyano esters (Table 14). An example is shown in Eq. 102.[207]



(Eq. 102)

α-Nitro Esters

Only a few α-nitro esters have been subjected to the Krapcho dealkoxycarbonylation (Table 15). An example is shown in Eq. 103.[126] The enantiomeric purity of the product was not reported.

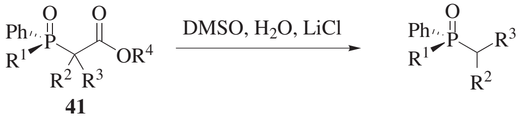


L4

(Eq. 103)

α-Phosphoryl Esters

The examples listed in Table 16 involve mostly chiral non-racemic phosphine oxides of type **41** (Eq. 104). Of note is that α,α-disubstituted esters are poor substrates for dealkoxycarbonylation (entry 1), that the bulky (−)-menthyl group is removed more readily than a methyl group (entries 2 and 3), and that no racemization on phosphorus takes place.

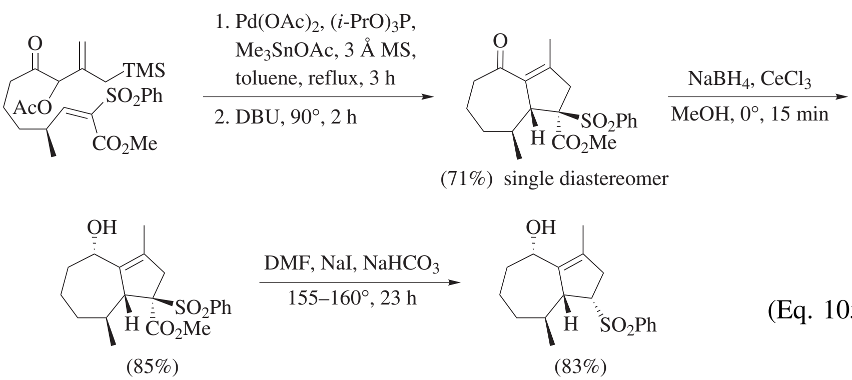


(Eq. 104)

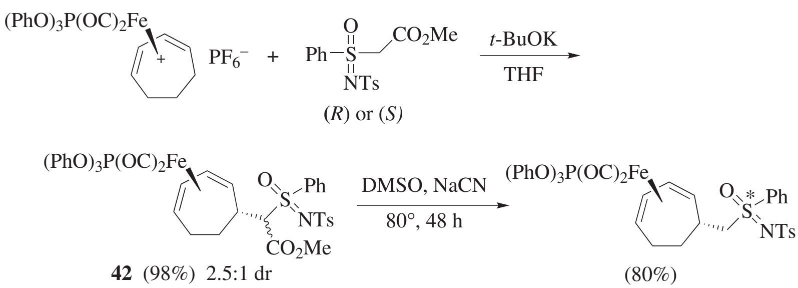
R^1	R^2	R^3	R^4	Temp	Time (h)	Yield (%)	Refs.
Me	Me	Me	Me	180º	6–18	14	208
Et	H	H	Me	180º	6–18	34	208
Et	H	H	(–)-menthyl	reflux	12	60	209
Et	Bn	H	(–)-menthyl	180º	6–18	67	103

α-Sulfonyl and α-Sulfoximino Esters

The Krapcho dealkoxycarbonylation of α-sulfonyl esters (Table 17) is specific for carboxylic esters in that no cleavage of a sulfonyl group under these conditions has been reported so far. Yields are usually good to excellent. An example is shown in Eq. 105.[210] The product configuration was assigned solely on the assumption that protonation of the intermediate enolate occurs from the less hindered side. Dealkoxycarbonylation of an α-sulfoximino ester (Table 17) is shown in Eq. 106.[211] Dealkoxycarbonylation of intermediate **42** (NaCN, DMSO, 120°) proceeds without racemization on sulfur.



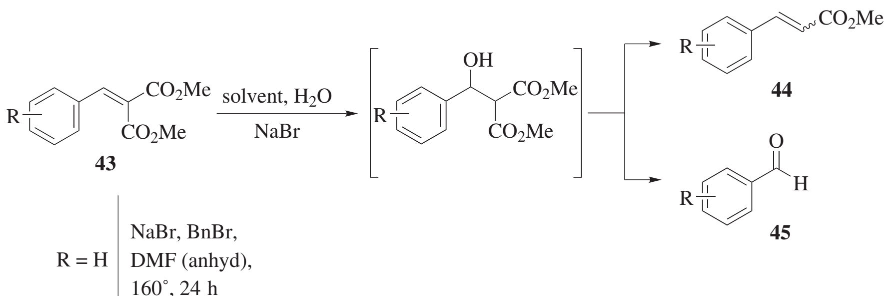
(Eq. 105)

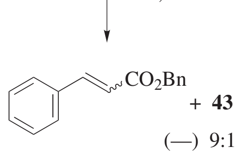


(Eq. 106)

Alkylidene Derivatives of Activated Esters

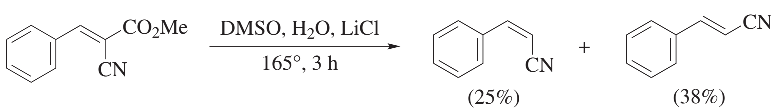
Alkylidene derivatives of a number of activated esters (Table 18) are dealkoxycarbonylated in yields that range from mediocre to excellent. A study of variously substituted benzylidenemalonates **43** (Scheme 20) concludes that the reaction proceeds by initial addition of water to the double bond followed by dealkoxycarbonylation, rather than via a vinyl carbanion.[212] The observation that the rate of dealkoxycarbonylation for *para*-substituted benzylidenemalonates decreases in the order NO_2 > H > Me > MeO, that *ortho* substituents decrease the rate and increase the amount of (*Z*)-cinnamates **44** formed, and that small amounts of benzaldehydes **45** are formed by a reverse Knoevenagel reaction all are considered evidence for the proposed mechanism. Moreover, attempts to trap the vinyl anions with benzyl bromide were unsuccessful (Scheme 20; see, however, Eq. 117). Dealkoxycarbonylation of (*E*)-methyl benzylidenecyanoacetate gives a 2:3 mixture of (*Z*)- and (*E*)-cinnamonitrile (Eq. 107).[213] The authors seem to consider the operation of both the water addition mechanism and one involving a vinyl carbanion as an intermediate in this case.





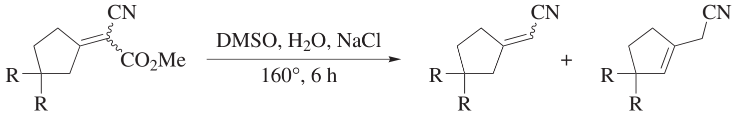
R	Solvent	Temp (°)	Time (h)	Yield (%) **44**	(*E*)/(*Z*)	**45**
H	DMF	153	23	90	92:8	0
H	DMSO	165	6	55	82:18	13
2-MeO	DMF	153	23	38	60:40	0
4-MeO	DMF	153	23	90	78:22	0

Scheme 20



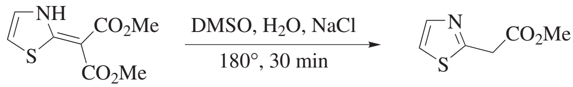
(Eq. 107)

Partial deconjugation of the double bond in the product is observed on occasion (nitrile **47** versus nitrile **46**, Eq. 108).[214] It becomes complete when the product of deconjugation is aromatic (Eq. 109).[215]



46 **47** (Eq. 108)

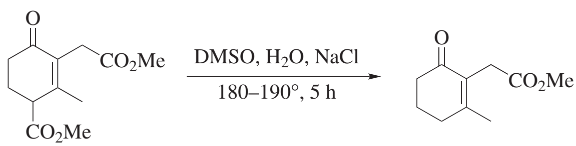
R	Yield (%) 46 + 47	46/47
H	55–65	3:1
Me	55–65	4:1



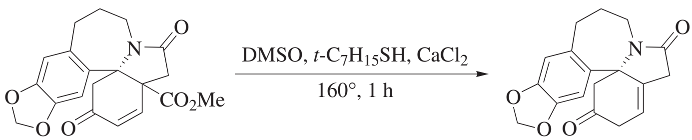
(48%) (Eq. 109)

Vinylogous and Phenylogous Activated Esters

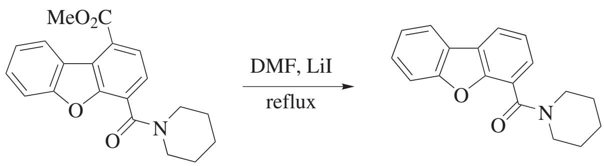
Dealkoxycarbonylations may also be carried out with substrates where the ester and the activating group are separated by one or more double bonds, including aromatic bonds (Table 19). When a non-aromatic double bond is involved, protonation of the intermediate dienolate may occur either at C_α or C_γ. Which type is observed depends on the substitution pattern (Eqs. 110[216] and 111[217]). The mercaptan in the latter reaction is added to prevent air oxidation of the dienolate; a bulky thiol is chosen in this case to minimize its addition to the substrate double bond. Dealkoxycarbonylation of an amido ester separated by a phenyl group is shown in Eq. 112.[218] A similar reaction of a nitro ester was mentioned previously (Scheme 11).



(70%) (Eq. 110)



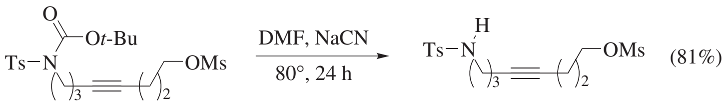
(83%) (Eq. 111)



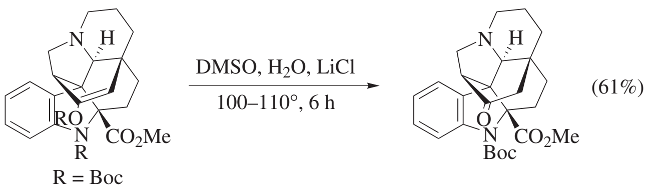
(59%) (Eq. 112)

Miscellaneous Reactions

In Table 20 are collected a few reactions that do not fit into the above-discussed categories and whose only common feature is that they are carried out under the conditions of the Krapcho dealkoxycarbonylation. Eq. 113 shows the selective cleavage of an *N*-Boc group,[219] whereas in Eq. 114 an *O*-Boc group is selectively removed in the presence of an *N*-Boc group.[220]



(Eq. 113)

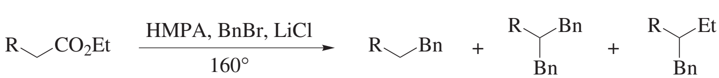


(Eq. 114)

Trapping of the Intermediate Enolates by Electrophiles Other Than a Proton

Attempts to intercept the enolate formed when activated esters are dealkoxycarbonylated in the presence of a salt (Scheme 4) by an external or internal electrophile other than a proton have met with mixed success.

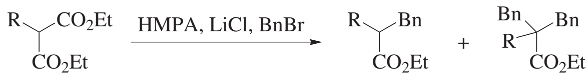
Alkylations (Table 21A). Trapping experiments with α-unsubstituted activated esters, using substoichiometric amounts of benzyl bromide, are shown in Eq. 115.[21] Mixtures of monoalkylated products **48** and dialkylated products **49** are formed except in the reaction involving ethyl acetoacetate. Product **50** arises from alkylation of the enolate by the ethyl bromide that is generated during the reaction. Yields, which are based on benzyl bromide, are unimpressive, and are even lower with the less reactive 1-octyl bromide. Similar dealkoxycarbonylative alkylations of monosubstituted malonates **51** (Eq. 116) proceed in better yield, to provide monoalkylated product **52** exclusively when R = NHAc, and a 7:1 mixture of monoalkylated product **52** and dialkylated product **52a** when R = *n*-Bu. The reaction of entry 1 is of interest in that the enolate can be generated selectively in the presence of the acidic NHAc group.[21] Only ester exchange, and no dealkoxycarbonylation, is observed when dimethyl α,α-dimethylmalonate is treated with benzyl bromide and lithium chloride in HMPA at 155° (Eq. 3).



(Eq. 115)

48 **49** **50**

R	Time (h)	Yield (%) **48**	**49**	**50**
EtO_2C	1	60	14	13
MeCO	1.5	24	0	—
NC	1	30	64	—

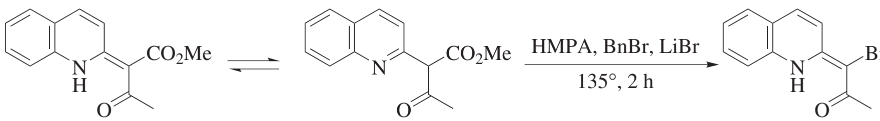


51 **52** **52a**

(Eq. 116)

			Yield (%)	
R	Temp (°)	Time (h)	**52**	**52a**
AcHN	150–160	1–1.5	52	—
n-Bu	155	1.5	71	10

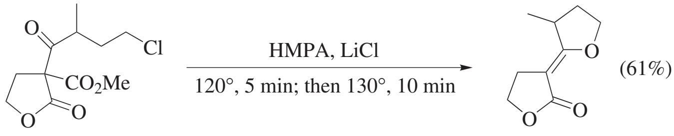
Isolation of the benzylation product **55** from the reaction of alkylidene β-keto ester **53** (Eq. 117)[221] is not conclusive evidence for the intermediacy of a vinyl carbanion since dealkoxycarbonylation could have proceeded by way of the tautomer **54**.



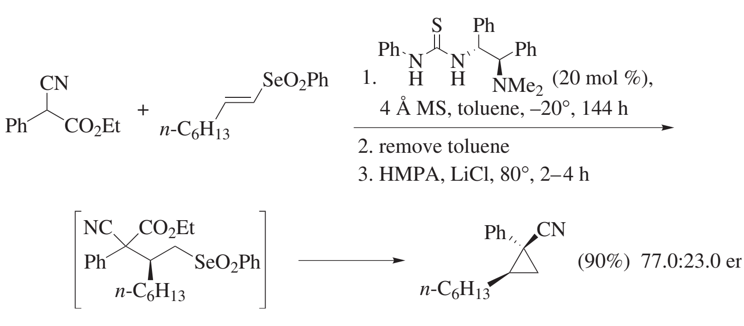
53 **54** **55** (37%)

(Eq. 117)

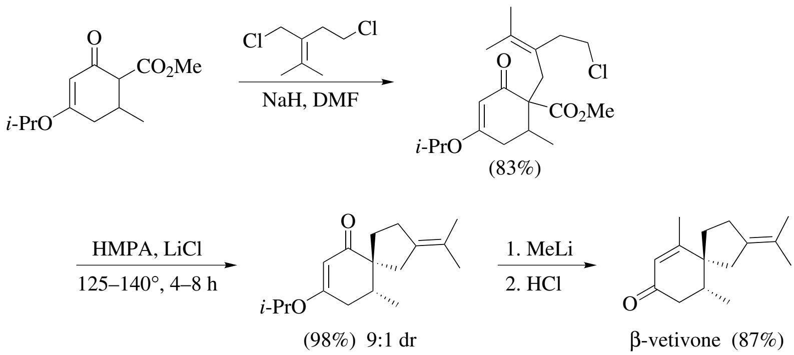
Cyclizations (Table 21B). Both intramolecular alkylations and intramolecular Michael additions have been reported and they show considerable promise. Examples of the former include *O*-alkylation (Eq. 118)[222] and *C*-alkylation (Scheme 21[223] and Eq. 119[224]). An intramolecular Michael reaction was mentioned earlier in Scheme 12; another (Eq. 120) shows that formation of five-membered rings proceeds well, providing a mixture of diastereomeric products **56** and **57**, whereas some uncyclized dealkoxycarbonylation product **58** is isolated in the cyclization leading to the six-membered product.[225] A comparison of the stereochemical outcome with that of the base-catalyzed cyclization of cyanide **58** was not reported. Intramolecular addition of the enolate oxygen to a cyano group subsequent to dealkoxycarbonylation has been observed in one case (9B-C_{17}).[199]



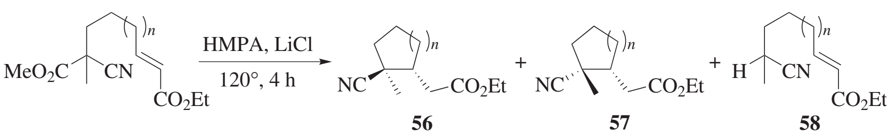
(Eq. 118)



(Eq. 119)



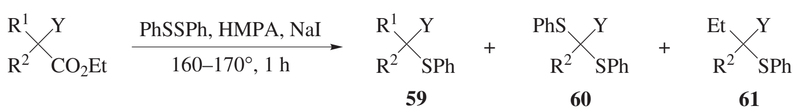
Scheme 21



n	Yield (%) 56 + 57 + 58	56/57/58
1	67	77:23:0
2	45	69:15:16

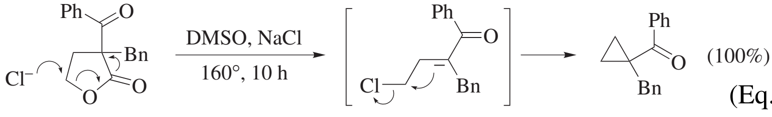
(Eq. 120)

Miscellaneous Reactions (Table 21C). Dealkoxycarbonylation of geminal diesters, β-keto esters, and α-cyano esters in the presence of diphenyl disulfide furnishes the α-thiophenyl derivatives **59** in fair to good yields (Eq. 121).[226] Some disulfenylation products (**60**) and alkylation by in situ formed EtI (product **61**) are also observed. Treatment of α-acyl lactones under Krapcho conditions gives acyl cyclopropanes. The suggested mechanism is shown in Eq. 122.[227]



(Eq. 121)

Y	R^1	R^2	Yield (%) 59	60	61
EtO_2C	H	n-Bu	40	0	0
EtO_2C	Bn	Bn	66	0	0
MeCO	H	H	67	8	0
NC	H	H	23	3	15

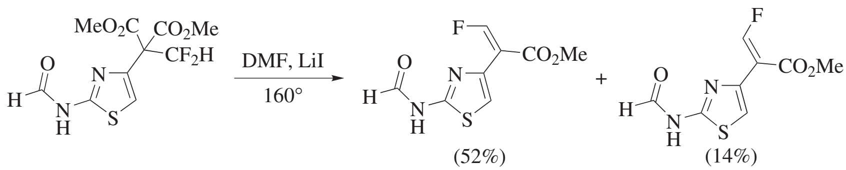


(Eq. 122)

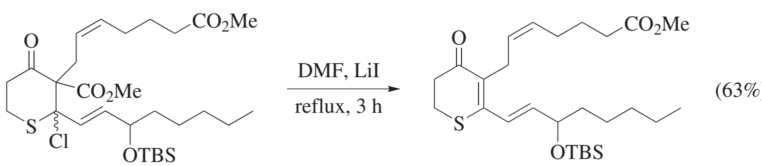
Functional Group Compatibility

The Krapcho dealkoxycarbonylation in general is tolerant of many functional groups. Exceptions are noted below. The distance of the functional group from the reaction center can be of crucial importance to the outcome of the reaction. Leaving groups in the β-position are usually eliminated to form a double bond. For the purpose of this discussion, a group attached to the carbon bearing the activated ester is considered to be α, etc. In geminal diesters, amino and hydroxy groups in a γ- or δ-position, even protected ones, may form lactams and lactones, respectively, with the remaining ester group.

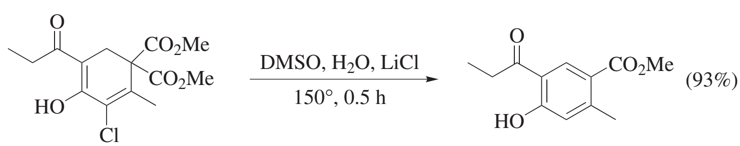
Halogens. α-Fluoro groups are stable (3-C_7[228]; 5-C_8[229]), but the elimination of a β-fluoro (Eq. 123)[230] and a β-chloro group (Eq. 124)[124] have been reported. Aromatization is the driving force in the elimination of the γ-chloro group depicted in Eq. 125.[231]



(Eq. 123)



(Eq. 124)



(Eq. 125)

Nitrogen Functional Groups. Amines may be used in the form of their hydrochlorides (Eq. 27). Free amino or acylamino groups in a γ- or δ-position may lead to the formation of lactams or imides, respectively, in the dealkoxycarbonylation of geminal diesters (Eq. 72; 2-C_{11};[175] 2-C_{13}[232]). The common nitrogen protecting groups such as Boc and Cbz are stable under Krapcho conditions. A β-trimethylammonium group undergoes a Hofmann elimination (Eq. 100).

β-Nitro groups are eliminated in geminal diesters, β-keto esters, α-cyano esters, and α-sulfonyl esters (Eq. 126).[233]

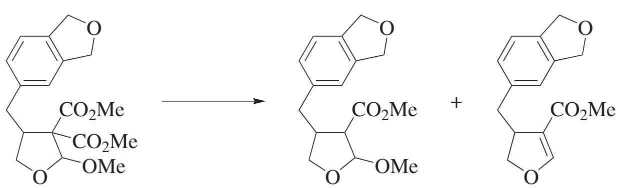
(Eq. 126)

Y	R^1	R^2	R^3	Temp (°)	Time (h)	Yield (%)
EtO_2C	Me	Me	Me	130–140	3	80
MeCO	Me	Me	*n*-Bu	130–140	4	60[a]
NC	$-(CH_2)_5-$		*i*-Pr	150	1	63[a]
$4\text{-}MeC_6H_4O_2S$	Me	Me	Me	130–140	2	87[a]

[a] The yield is for two steps.

Oxygen Functional Groups. α-Hydroxy groups are tolerated (11C-C_{21}).[234] The presence of γ- or δ-hydroxy groups may lead to lactone formation if the rings so formed are strain-free (see discussion in connection with Eq. 69). Lactone formation with a γ-hydroxy group instead of dealkoxycarbonylation has been observed with an α-cyano ester (13A-C_{12}).[235]

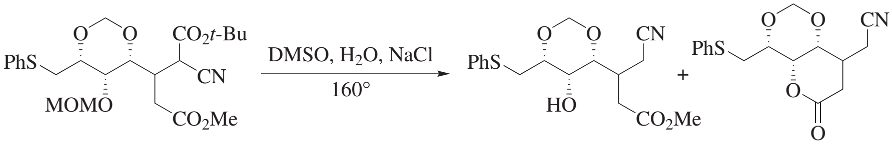
Ethers, including OBn and *O*-trityl groups, are usually stable, except one report is known of the partial elimination of a β-methoxy group under standard Krapcho conditions (Eq. 127).[236] Only the elimination product **63** is obtained in the presence of trifluoroacetic acid. Cleavage of a methoxy group attached to an aromatic ring when *N*-methylpyrrolidinone is used in place of DMF as the solvent has been reported once (11A-C_{10-15}).[237] Cleavage of a methoxymethoxy (MOMO) group δ to an ester group that is not involved in the dealkoxycarbonylation followed by partial lactone formation has also been observed in one reaction (Eq. 128).[238] Silyl ethers as a rule are stable, but one example of a δ-OTMS group being cleaved with concomitant formation of a lactone (Eq. 129)[239] and one instance where an OTIPS group is partially cleaved (Eq. 141) are known. *O*-*tert*-Butyldimethylsilyloxy groups are cleaved when $MgCl_2{\bullet}6H_2O$ is used as the salt additive (11A-C_9;[240] 11A-C_{10}[240]) and partial cleavage of this protecting group (LiI, DMF) can be minimized by addition of a phosphate buffer (11B-C_{21}).[124] Elimination of an OTBS group to form a double bond under unspecified conditions has also been reported (8B-C_{12}).[241] A β′-mesyl group is eliminated during the dealkoxycarbonylation of a vinylogous β-keto ester (Scheme 23); the yield is much lower when the corresponding β-hydroxy analog is used.



(Eq. 127)

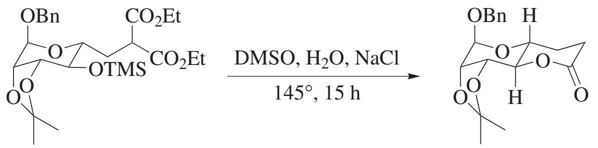
62 **63**

DMSO, NaCl, 130°	**62** + **63** (50%), **62**/**63** = 1:1
NMP, TFA, LiCl, Mw, 180°, 5 min	**63** (79%)



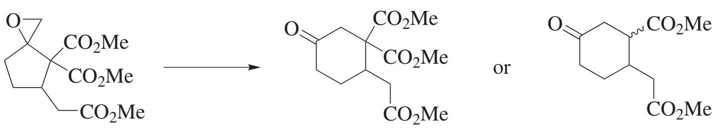
(72–78%) 1:1

(Eq. 128)



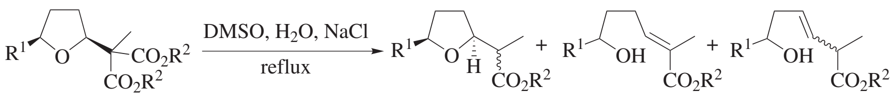
(70%) (Eq. 129)

The only β,γ-epoxy activated ester subjected to the Krapcho dealkoxycarbonylation forms product **65** through initial ring expansion to the six-membered keto compound **64** (Eq. 130).[242] Extensive ring opening occurs in the reaction of an α-tetrahydrofurylmalonate under standard Krapcho conditions to afford a mixture of the desired product **66** and alcohols **67** and **68**, whereas a closely related substrate reacts normally (Eq. 131). The difference may be that dealkoxycarbonylation of the ethyl ester requires much longer reaction times in this case. A THP group in the δ-position is cleaved with the formation of δ-lactones (Eq. 70), whereas such groups at a more distant location are unaffected (2-C_9;[245] 3-C_8[145]).



64 **65** (Eq. 130)

CH_2Cl_2, LiI, rt, 24 h **64** (90%)
DMSO, LiI, 130° **65** (50%)



66 **67** **68**

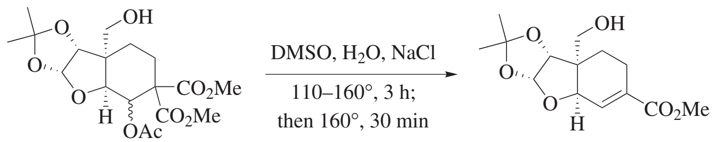
R^1	R^2	Time (h)	Yield (%) **66**	**67**	**68**	Refs.
H	Et	30	30	38[a]	7	243
(*R*)-MeCH(OH)CH_2	Me	3	78[b]	0	0	244

[a] A 96:4 mixture of (*E*)/(*Z*) isomers is formed.
[b] A 1:1 mixture of diastereomers is formed.

(Eq. 131)

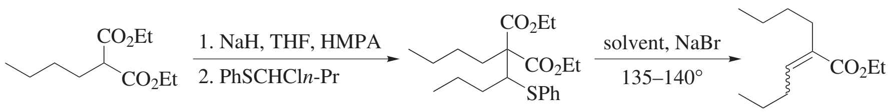
Ketals, including acetonides, are stable except when $MgCl_2{\bullet}6H_2O$ is used as the salt additive, in which case cleavage with lactone formation may be observed (Scheme 14). Cleavage of a dimethyl acetal instead of dealkoxycarbonylation has been reported in one case (8C-C_{18}).[246]

A β-acetoxy group is eliminated (Eq. 132)[247] and partial hydrolysis (DMSO, H_2O, LiCl) of a distal acetoxy group at 190°, but not at 160°, has been observed (3-C_{10}).[144]



(47%) (Eq. 132)

Sulfur and Selenium Functional Groups. β-Phenylthio groups are eliminated during dealkoxycarbonylation in a general synthesis of α-substituted acrylates (Eq. 133).[248] However, β-RS groups (R = alkyl, aryl) are not eliminated (DMSO, H_2O, NaCl, reflux) when attached to a cyclopropane ring (4A-C_7).[249] Partial elimination of a β-butylthio group is observed in the reaction of a cyclic β-keto ester (6A-C_7).[250] γ-Phenylthio groups are not affected in Krapcho dealkoxycarbonylations (11A-C_7;[251] 11A-C_{8-10}[252]).

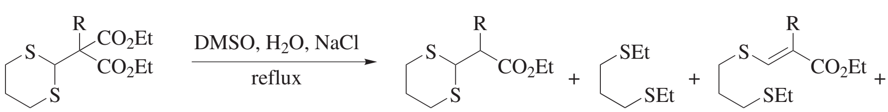


Solvent	Time (h)	Yield (%)[a]	(*E*)/(*Z*)
DMF	10	70	90:10
HMPA	5	72	79:21

[a] The yield is for 3 steps

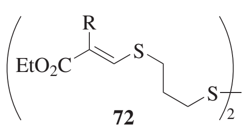
(Eq. 133)

Thioacetals of α-formyl malonates are extensively ring-opened (forming products **70**–**72**) if the α-carbon carries an additional substituent; however, the desired product **69** is obtained in excellent yield when R = H (Eq. 134).[243] More distant thioacetals (3-C_{10})[253] and thioketals (2-C_{11})[254] are not cleaved during dealkoxycarbonylations.



69 **70** **71**

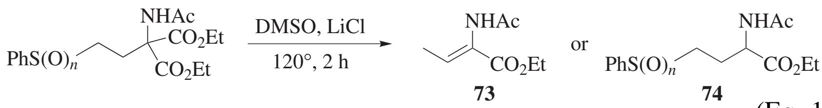
R	Time (h)	Yield (%) **69**	**70**	**71**	**72**
H	0.5	95	0	0	0
Me	4	10	10	38	38
Ph	2	17	9	34	17



72

(Eq. 134)

A geminal diester containing a γ-phenylsulfinyl group undergoes elimination/double bond isomerization as well as dealkoxycarbonylation (product **73**), whereas the corresponding phenylsulfonyl derivative is only dealkoxycarbonylated (product **74**) (Eq. 135).[255] β-Phenylsulfinyl and β-arylsulfonyl groups remain intact when attached to a cyclopropane ring (4A-C_5;[256] 4A-C_7[249]).

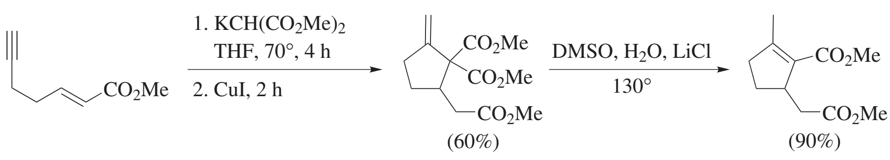


(Eq. 135)

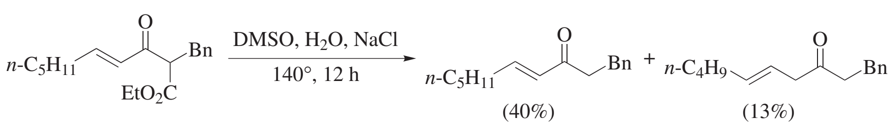
$n = 1$ **73** (38%)
$n = 2$ **74** (88%)

Phenylselenyl groups, even when attached to the β-position (11B-C_{7-11}),[257] remain unchanged during dealkoxycarbonylations.

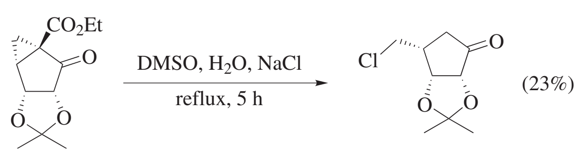
Carbon Functional Groups. Double bond isomerization under the conditions of the Krapcho dealkoxycarbonylation takes place on occasion. An example was discussed previously (Scheme 16) where lowering the reaction temperature prevents this side reaction. In the example shown in Eq. 136,[258] isomerization to the endocyclic α,β-unsaturated ester proceeds under relatively mild conditions. Partial deconjugation is observed in the dealkoxycarbonylation of a γ,δ-unsaturated β-keto ester (Eq. 137).[259] Partial (Eq. 108) or complete (Eq. 109) deconjugation may also be observed in the dealkoxycarbonylation of alkylidene derivatives of activated esters. Attempted dealkoxycarbonylation of the bicyclo[3.1.0] derivative shown in Eq. 138 proceeds with chloride-induced ring opening of the cyclopropane.[251] Treating the isomer where the ester and acetonide are *cis* under the same reaction conditions gives the expected product, also in low yield (18%).



(Eq. 136)

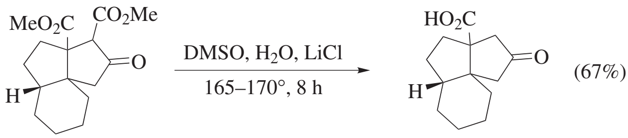


(Eq. 137)



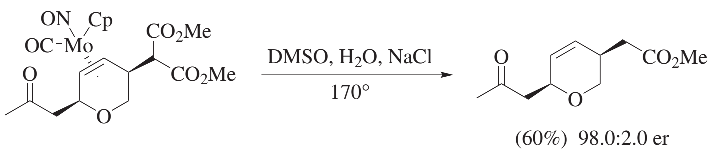
(Eq. 138)

Ester groups not involved in the dealkoxycarbonylation, including *tert*-butyl ones, are usually unaffected, but hydrolysis to the acid is observed on rare occasions (Eq. 139).[260]



(Eq. 139)

Miscellaneous Functional Groups. Carbon−silicon bonds, even in the β-position (11A-C_6),[261] are not cleaved. An arene iron (2-C_9,[147] 160°) and two diene iron complexes (Eq. 106, 80°; 2-C_{11},[262] 95°) remain intact during a Krapcho dealkoxycarbonylation, but a molybdenum mono-ene complex is decomplexed at 170° (Eq. 140).[263] Trialkyltin substituents survive (Eq. 42).



(Eq. 140)

APPLICATIONS TO SYNTHESIS

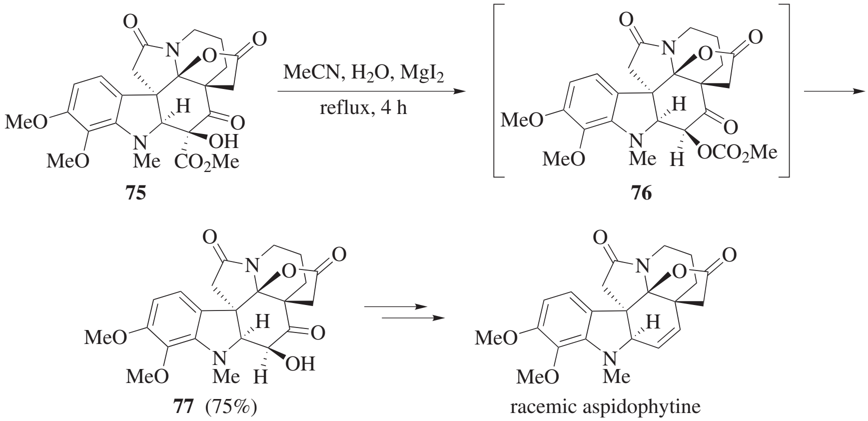
The Krapcho dealkoxycarbonylation has found frequent use in the preparation of both natural and other products. Deuterium may be introduced by carrying out the dealkoxycarbonylation in deuterium oxide (Scheme 9; 2-C_5[264]). General syntheses of 1-arylcyclopropyl cyanides (Eq. 119), α,β-unsaturated esters, ketones, nitriles, and sulfones (Eq. 126) and α-substituted acrylates (Eq. 133) were mentioned earlier, as were syntheses of (*R*)-muscone (Eq. 91) and β-vetivone (Scheme 21).

Racemic Aspidophytine

The α-hydroxy β-keto ester **75** undergoes demethoxycarbonylation on treatment with magnesium iodide and water in acetonitrile to give the α-hydroxy ketone **77** in 75% yield (Scheme 22).[265] This transformation is not a typical Krapcho demethoxycarbonylation since carbonate **76** was shown to be the first intermediate. Treatment of ester **75** under standard conditions (DMSO, H_2O, NaCl, reflux, 4 h) also furnishes product **77**, albeit in much lower yield (20%). Further manipulation leads to racemic aspidophytine.

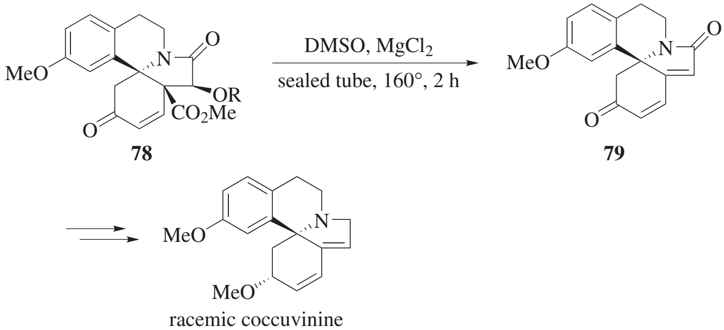
Racemic Coccuvinine

Coccuvinine has been isolated from the plant *Cocculus laurifolius DC* and shows hypotensive and neuromuscular blocking action. Treatment of tetracyclic vinylogous β-keto ester **78** (R = Ms) with DMSO and $MgCl_2$ in a sealed tube leads to the demethoxycarbonylative elimination product **79** (Scheme 23).[266] With the poorer hydroxyl (R = H) leaving group, the yield is much lower.



75 → [76] → 77 (75%) → racemic aspidophytine

Scheme 22



78 → 79 → racemic coccuvinine

R	Yield (%)
H	32
Ms	89

Scheme 23

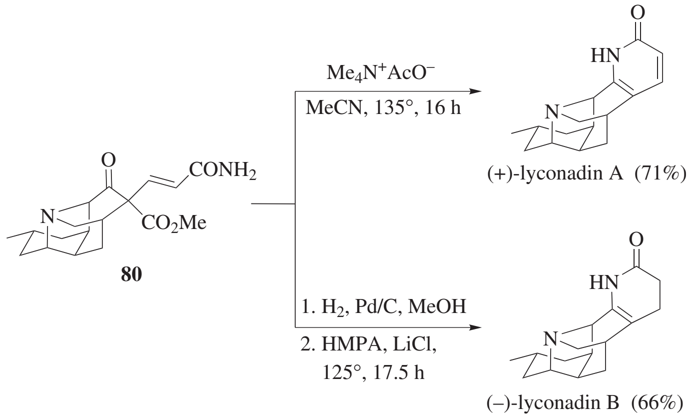
(+)-Lyconadin A and (−)-Lyconadin B

These alkaloids with an unusal pentacyclic ring skeleton are isolated from the club moss *Lycopodium complanatum*. Intermediate **80** serves as a precursor for both target compounds via a tandem dealkoxycarbonylation/cyclization (Scheme 24).[267]

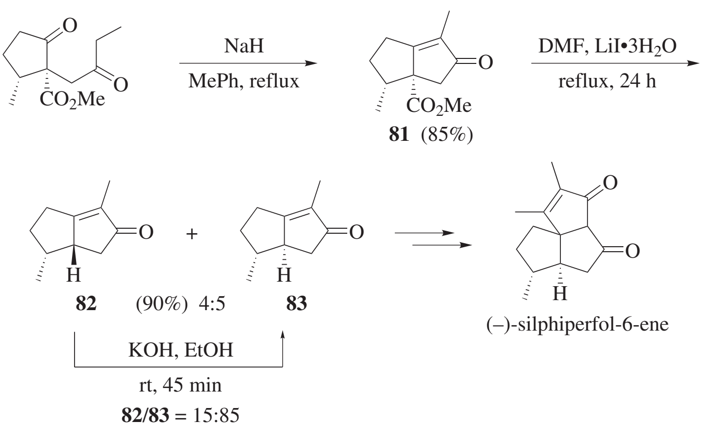
(−)-Silphiperfol-6-ene

(−)-Silphiperfol-6-ene is an angular triquinane sesquiterpene isolated from the roots of *Siphium perfoliatum.* Krapcho dealkoxycarbonylation of the vinylogous β-keto ester **81** affords an epimeric mixture of enones **82** and **83**. The mixture is enriched in the desired epimer by equilibration with base, which proceeds without loss of enantiomeric purity (Scheme 25).[268–270] Subsequent transformations of enone **83** lead to (−)-silphiperfol-6-ene.

In addition, syntheses of (−)-morphine,[271] (−)-secodaphniphylline,[272] racemic magellanine,[273] (+)-paspalicine,[274] racemic coccinelline,[275] (−)-strychnine,[276]



Scheme 24



Scheme 25

(+)-maritimol,[277] (+)-γ-lycorane,[278] a number of pheromones,[279–281] and a defensive substance from a termite soldier,[282] among others, have used key intermediates prepared via dealkoxycarbonylations of various substrates.

COMPARISON WITH OTHER METHODS

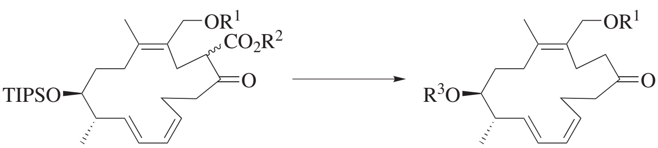
Selective entries describing a number of other methods for effecting dealkoxycarbonylations are included in the Tabular Survey. More classical procedures using aqueous acidic or basic hydrolysis are not included in the survey or in the discussion below.

Inorganic Salts in Other Solvents

Dealkoxycarbonylation of β-keto esters has been accomplished on occasion in non-traditional solvents such as acetonitrile, THF, or diglyme. An example was given earlier (Scheme 22), where the Krapcho method proceeds with poor yield. Yields are generally good and reaction temperatures are often considerably lower.

Lithium Iodide/Pyridine Bases

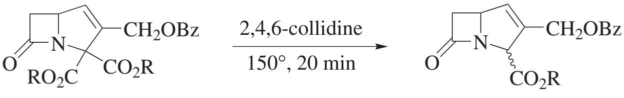
Treatment of esters with lithium iodide in pyridine bases such as pyridine itself (bp 115°), 2,4-dimethylpyridine (2,4-lutidine, bp 159°), 2,6-dimethylpyridine (2,6-lutidine, bp 154°), or 2,4,6-trimethylpyridine (2,4,6-collidine, bp 171°), usually at reflux, results in their cleavage to the carboxylic acids.[283,284] The temperature is high enough that activated esters undergo decarboxylation,[285] resulting in a net dealkoxycarbonylation. The reaction has been applied mostly to β-keto esters, both acyclic and cyclic, as well as hindered ones. The preparation of 2-benzylcyclopentanone from methyl 1-benzyl-2-oxocyclopentanecarboxylate is described in *Organic Syntheses*.[286] Mostly methyl esters are used but examples exist of ethyl, *tert*-butyl (Eq. 141), benzyl, and *p*-nitrobenzyl esters (Eq. 142).[289] The latter case is a rare example where this method is applied to a geminal diester. It is of note that the remaining ester group is not cleaved, even though the temperature is fairly high.



84 R^3 = TIPS
85 R^3 = H

R^1	R^2	Conditions	Yield (%) **84**	**85**	Refs.
Me	*t*-Bu	2,4,6-collidine, LiI•$2H_2O$, 100°, 15 h	73	0	287
PMB	Me	DMSO, H_2O, NaCN, 125°, 6 h	68	12	288

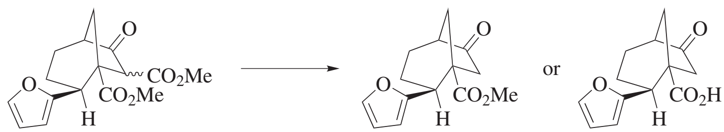
(Eq. 141)



(52%) (Eq. 142)

R = 4-$O_2NC_6H_4CH_2$

Although isolated ester groups in β-keto esters have been observed to hydrolyze to the acids at elevated temperatures in a number of reactions (Eq. 143),[290] many examples exist where such esters remain intact even at elevated temperatures (Eq. 143).[290] Where comparisons are possible, yields of this method are similar to those obtained with the Krapcho dealkoxycarbonylation as shown in Eq. 141, where the latter gives a somewhat higher overall yield but also results in partial cleavage of a protecting group.

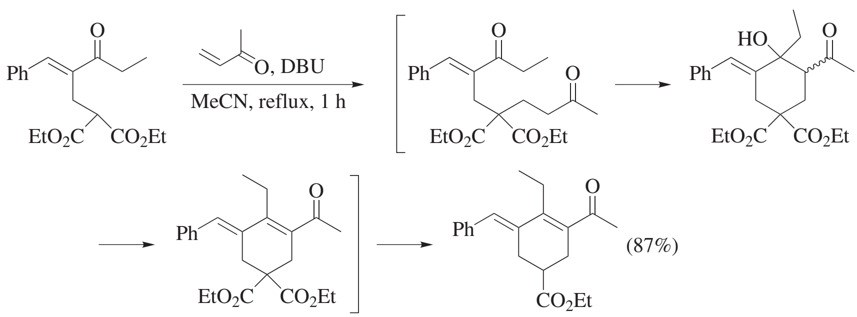


86 **87** (Eq. 143)

pyridine, LiI, 115°, 2 d — **86** (97%)
2,4,6-collidine, LiI, 140°, 4 h — **87** (25%)

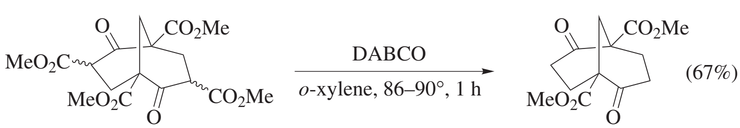
Amines

The bicyclic base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) dealkoxycarbonylates geminal diesters in refluxing *o*-xylene.[291,292] Extended reaction times lead to cleavage of the remaining ester group to the acid. The homolog 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[293] and 3-quinuclidinol (1-azabicyclo[2.2.2] octan-3-ol)[291,294] have also seen limited use in this context, but it appears that the former is suitable for the dealkoxycarbonylation of geminal diesters (Scheme 26)[295] and β-keto esters (11A-C_{15}).[296]



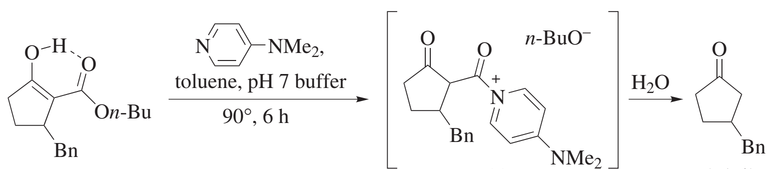
Scheme 26

The tertiary amine base that has been employed more frequently is 1,4-diazabicyclo[2.2.2]octane (DABCO).[291,297] This reagent dealkoxycarbonylates geminal diesters and β-keto esters in boiling aromatic hydrocarbons, usually *o*-xylene. The yields are comparable or somewhat lower than those obtained with the Krapcho method with which it is suggested to share the same mechanism.[297] Hindered geminal diesters give higher yields than unhindered ones because of formation of unidentified higher-boiling condensation products from the latter. The method is claimed to be selective for β-keto esters having at least one α-hydrogen based on the reaction shown in Eq. 144.[297] However, a vinylogous β-keto ester with a methyl group in the α-position (19-C_{17})[298] and α,α-disubstituted malonates (3-C_{5-25})[291] are dealkoxycarbonylated by DABCO, so that the failure of all carbomethoxy groups to be eliminated in the reaction of Eq. 144 may be due to the reluctance to form bridgehead enolates.

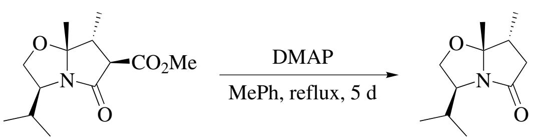


(Eq. 144)

Enolizable β-keto esters are dealkoxycarbonylated in toluene by the action of 4-dimethylaminopyridine (DMAP) and water (Eq. 145).[87] The intermediate pyridinium species **88** is suggested to be attacked by water to generate the corresponding β-keto acid which then spontaneously loses carbon dioxide to give the observed product. The methyl and *n*-butyl esters react at equal rates. The rates of dealkoxycarbonylation of a series of β-keto esters correlates with their enol contents, indicating that hydrogen bonding to the ester carbonyl group activates it for reaction with DMAP in the rate-determining step. Unspecified non-enolizable β-keto esters and the acyclic β-keto ester ethyl 7-acetoxy-2-acetyl-5-methylheptanoate are not dealkoxycarbonylated under these conditions. Malonates were also reported to be unreactive but it was subsequently shown that they do react at higher temperatures (refluxing *p*-xylene) and extended reaction times of 3 to 6 days (2-C_{13-14}).[299] The original authors emphasized that water needed to be present but some later workers use anhydrous conditions.[295,300] Eq. 146 shows an application of this method where others, including the Krapcho dealkoxycarbonylation, lead to decomposition, suspected to be due to formation of an acyliminium species.[301]

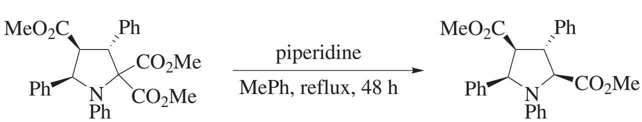


88 (71%) (Eq. 145)



(51%) (Eq. 146)

Piperidine in refluxing anhydrous solvents such as acetonitrile or toluene dealkoxycarbonylates geminal diesters,[302] β-keto esters,[303] and α-cyano esters[302] with formation of *N*-alkylpiperidines as additional products. Long reaction times are required and amide formation, rather than dealkoxycarbonylation, is a serious side reaction in some cases, especially with ethyl esters. The method has not found much application so far. It appears to work best with α,α-disubstituted geminal dimethyl esters (Eq. 147).[302]

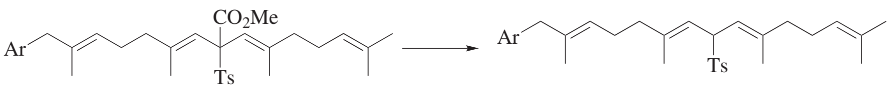


(72%) (Eq. 147)

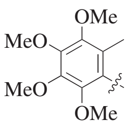
Thiolates

Activated esters are dealkoxycarbonylated by the action of 4-aminothiophenol and catalytic amounts of cesium carbonate in DMF at temperatures of 80–100°.[304]

Methyl esters react much faster than ethyl esters. When applied to geminal diesters, partial cleavage of the remaining ester group to the acid is observed. Yields in the example of Eq. 148 are superior to those obtained with the Krapcho method but they are comparable in the one other example where a direct comparison is possible (2-C_{10};[304] 2-C_{10-11}[305,306]). The method has not found widespread use to date.



Ar =



Conditions	Yield (%)
4-$H_2NC_6H_4SH$, Cs_2CO_3, DMF, 85°, 1 h	98
PhSH, Cs_2CO_3, DMF, 85°, 1 h	73
NaCl, DMF, 153°, 15 h	26
$Me_4N^+AcO^-$, HMPA, 100°, 7 h	62

(Eq. 148)

Deallyloxycarbonylation and Debenzyloxycarbonylation

Activated esters are deallyloxycarbonylated with formic acid and tertiary amines under palladium-catalysis[307,308] at room temperature to 100° (Eq. 149). The Krapcho method (ethyl ester, LiCl, wet DMSO) gives recovered starting material, but a similar substrate, under somewhat modified Krapcho conditions, leads to the desired product in fair yield (Eq. 149). The mild conditions of the palladium-mediated dealkoxycarbonylation of allyl esters gives it an advantage compared to other methods, including the Krapcho dealkoxycarbonylation, but this has to be weighed against the need for the additional step(s) required to prepare the substrate. Also, geminal diallyl esters give the acid by deallylation of the remaining ester group. Since the ester is usually the target in these cases, the product must be re-esterified, or the reaction has to be carried out with a mixed allyl alkyl ester.

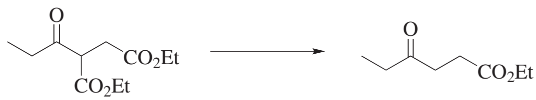
(Eq. 149)

R^1	R^2	Conditions	Yield (%)	Refs.
3,4-(OCH_2O)C_6H_3	allyl	$Pd(OAc)_2$, Ph_3P, HCO_2H, Et_3N, rt, 18 h	72	309
3,4-(OCH_2O)C_6H_3	Bn	H_2, Pd/C, EtOAc, rt, 1 h	53	309
2-furyl	Me	NMP, H_2O, LiCl, HOAc, reflux	48	237
n-Bu	Me	Al_2O_3, H_2O, dioxane, reflux, >200 h	0	310

Catalytic hydrogenolysis of β-keto benzyl esters produces the β-keto acids which often spontaneously lose carbon dioxide to give the ketones as illustrated in Eq. 149. In some cases heating is required to effect decarboxylation. Other hydride sources, such as W-2 Raney nickel, have also been used.

Miscellaneous Methods

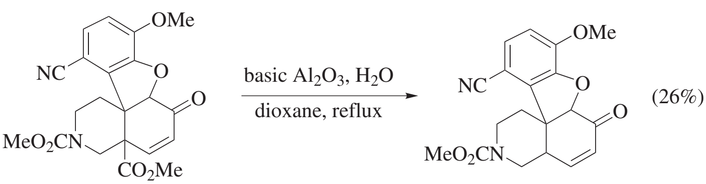
Malonates[311] and β-keto esters[312] are dealkoxycarbonylated by fusion with boric acid or boron oxide. The example shown in Eq. 150 is published in *Organic Syntheses*. The yield in this instance is somewhat lower than that achieved with the Krapcho method. In the other example where direct comparison is possible, boric acid gives somewhat higher yields (2-C_6).[311,315] This method has been applied to a few other substrates (9B-C_6;[316] 9B-C_{12};[317] 11B-C_{14-15}[318]).



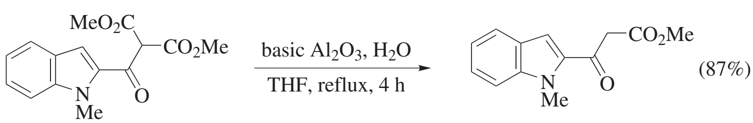
(Eq. 150)

Conditions	Yield (%)	Refs.
H_3BO_3 (1 equiv), 150°, 1.5 h	82–85	313
DMSO, H_2O, reflux, 4 h	95	314

Basic aluminum oxide in refluxing dioxane and water dealkoxycarbonylates β-keto esters.[310] This was the only method that gave any desired product, albeit in low yield, in the attempted dealkoxycarbonylation of the vinylogous β-keto ester shown in Eq. 151.[319] The method fails with hindered β-keto esters (Eq. 149; 11B-C_{9-13}[124]), but it has been applied successfully to the dealkoxycarbonylation of an acyl malonate (Eq. 152).[320] It is noteworthy that the product β-keto ester remains intact at the lower temperature of refluxing THF.



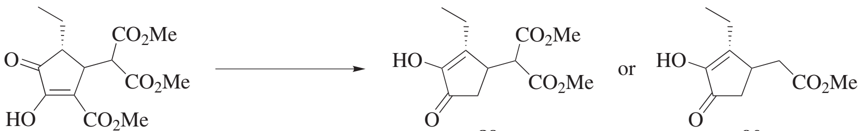
(Eq. 151)



(Eq. 152)

Geminal diesters and β-keto esters are dealkoxycarbonylated by heating with high-boiling carboxylic acids, such as stearic acid, in the presence of catalytic amounts of a phosphonium salt.[321] The Krapcho dealkoxycarbonylation gives consistently higher yields where a comparison is possible, and the method does not appear to have been applied by other workers. However, it might be useful for the preparation of lower-boiling products since they can be distilled directly from the reaction mixture without the need of an isolation procedure.

Refluxing carboxylic acids without any addends dealkoxycarbonylate a number of malonates and β-keto esters.[322] In the example shown in Eq. 153, refluxing acetic acid (bp 117°) only removes the ester group of the β-keto ester to afford product **89**, whereas in the higher-boiling propionic acid (bp 141°) both activated ester groups are cleaved to afford product **90**. No further applications of this method were found in the literature.



89 **90**

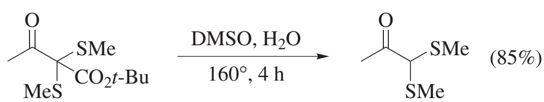
$MeCO_2H$, reflux, 26 h	**89** (80%)	(Eq. 153)
$EtCO_2H$, reflux, 72 h	**90** (60%)	

EXPERIMENTAL CONDITIONS

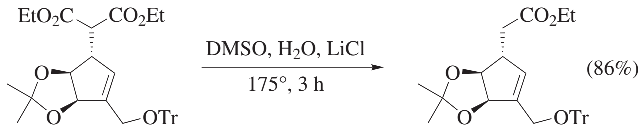
CAUTION: Dimethyl sulfoxide readily penetrates the skin. Impervious gloves must be worn when handling DMSO, especially its solutions, to prevent substances of unknown hazards from being transported into the body. Hexamethylphosphoric triamide is a suspected human carcinogen. Cyanides are highly toxic.

The various reaction parameters are discussed in the Scope and Limitations section. Reactions are generally performed in a flask equipped with a magnetic stir bar, a condenser, and a gas bubbler to vent the carbon dioxide and other volatiles formed during the reaction and to monitor its progress. Quantitative evolution of CO_2 does not occur, since the hydroxide formed by protonation of the enolate reacts with CO_2 gas to produce carbonates. Use of an inert atmosphere (nitrogen or argon) has been recommended for reactions involving salts in order to prevent oxidation of the intermediate enolates. Sealed tubes have also been employed but *to prevent explosions, these should be limited to very small-scale reactions.* Moreover, volatile alkyl halides formed in the reaction cannot escape and may alkylate the enolate (Scheme 6).

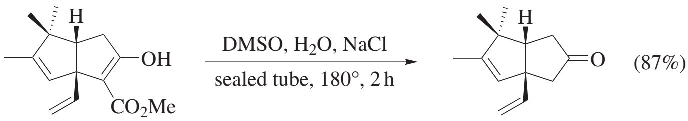
EXPERIMENTAL PROCEDURES



1,1-bis(Methylthio)-2-propanone [Dealkoxycarbonylation of an α,α-Disubstituted β-Keto *tert*-Butyl Ester in DMSO/Water].[323] A solution of *tert*-butyl 2,2-bis(methylthio)acetoacetate (19.9 g, 77 mmol) and 1.43 mL (77 mmol) of water in 100 mL of DMSO was heated at 160° for 4 h. After the cooled mixture was extracted with CH_2Cl_2 (3 × 100 mL), the combined extracts were washed with water, dried (Na_2SO_4), and concentrated. The residue was bulb-to-bulb distilled (bp 60°/0.1 mm) to give the title product as a pale-yellow oil (9.8 g, 85%): IR (CCl_4) 1720 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.37 (s, 1H), 2.36 (s, 3H), 2.08 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.45, 60.70, 25.72, 11.62. Anal. Calcd for $C_5H_{10}OS_2$: C, 39.97; H, 6.71. Found: C, 39.62; H, 6.71.

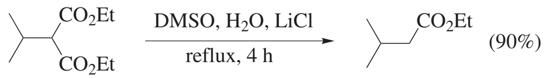


Ethyl 2-(3a*S*,4*R*,6a*R*)-6-(Trityloxymethyl)-2,2-dimethyl-4,6a-dihydro-3a*H*-cyclopenta[*d*][1,3]dioxol-4-yl)acetate [Dealkoxycarbonylation of an α-Monosubstituted Diethyl Malonate with DMSO and LiCl].[324] To a solution of diethyl 2-(3a*S*,4*S*,6a*R*)-6-(trityloxymethyl)-2,2-dimethyl-4,6a-dihydro-3a*H*-cyclopenta[*d*][1,3]dioxol-4-yl)malonate (7.5 g, 13.4 mmol) in DMSO (50 mL) were added LiCl (1.67 g, 39.4 mmol) and water (2 drops). The mixture was heated at 175° for 3 h, cooled, water (50 mL) was added, and the mixture was extracted with EtOAc (2 × 200 mL). The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/EtOAc (9:1) as eluent to afford the title product (5.7 g, 86%) as a white solid: mp 119°; $[\alpha]^{25}_{D}$ − 58 (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 6H), 7.30–7.20 (m, 9H), 5.86 (s, 1H), 5.01 (d, J = 5.5 Hz, 1H), 4.48 (d, J = 5.5 Hz, 1H), 4.15 (q, 2H), 3.83 (d, J = 14.5 Hz, 1H), 3.65 (d, J = 14.5 Hz, 1H), 3.18 (t, J = 6 Hz, 1H), 2.40 (dd, J = 2.0, 7.5 Hz, 2H), 1.36 (s, 3H), 1.31 (s, 3H), 1.26 (t, J = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 144.0, 142.7, 128.6, 128.2, 127.8, 127.0, 110.6, 86.9, 84.5, 83.7, 61.4, 60.6, 47.3, 38.0, 27.6, 26.1, 14.2; HRMS–ESI (m/z): $[M + H]^+$ calcd for $C_{32}H_{34}O_5$, 499.2484; found, 499.2478.

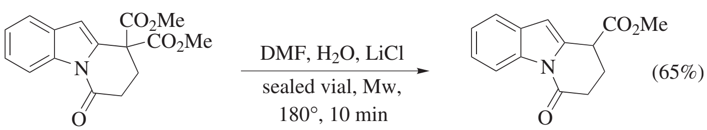


91

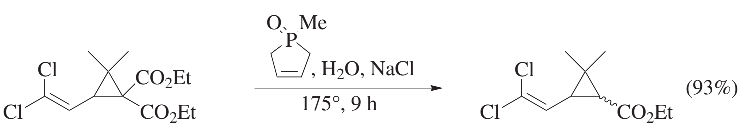
(1*S*,5*R*)-6,6,7-Trimethyl-1-vinylbicyclo[3.3.0]oct-7-en-3-one [Dealkoxycarbonylation of a Cyclic β-Keto Methyl Ester in a Sealed Tube].[325] A solution of the β-keto ester **91** (tautomeric mixture, 180 mg, 0.73 mmol), NaCl (126 mg, 2.18 mmol), DMSO (2 mL), and water (0.01 mL), contained in a sealed Carius tube, was heated at 180° for 2 h. The reaction mixture was cooled to rt, diluted with Et_2O (10 mL), washed with water (5 mL) and brine (5 mL), and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using hexane/EtOAc (19:1) as eluent furnished the title product (120 mg, 87%) as an oil: R_f (hexane/EtOAc 19:1) 0.5; $[\alpha]^{23}_{D}$ − 46.1 (*c* 4.4, $CHCl_3$); IR (neat) 3080, 2960, 1743, 1632, 1442, 1400, 1175, 1000, 911, 837 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3/CCl_4$ 1:1) δ 5.98 (dd, J = 17.3, 10.4 Hz, 1H), 5.24 (s, 1H), 4.97 (d, J = 17.3 Hz, 1H), 4.95 (d, J = 10.4 Hz, 1H), 2.45–2.20 (m, 5H), 1.66 (s, 3H), 1.08 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CHCl_3/CCl_4$ 1:1) δ 218.0, 148.0, 145.8, 128.1, 111.7, 56.3, 56.0, 48.6, 48.3, 40.2, 28.4, 23.3, 12.5; HRMS (m/z): $[M + Na]^+$ calcd for $C_{13}H_{18}ONa$, 213.1255; found, 213.1263.



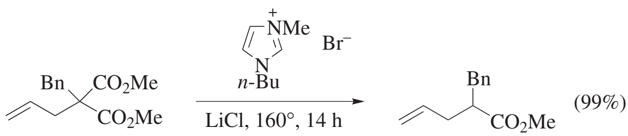
Ethyl 3-Methylbutanoate [Dealkoxycarbonylation of an α-Mono-substituted Diethyl Malonate with DMSO and LiCl and Direct Distillation of the Product from the Reaction Mixture].[15] In a 100-mL round-bottom flask, equipped with a magnetic stir bar and a reflux condenser, were placed diethyl isopropylmalonate (6.1 g, 30 mmol), water (0.5 mL, 28 mmol), LiCl (2.5 g, 60 mmol), and DMSO (50 mL), and the mixture was heated under reflux for 4 h. The reflux condenser was replaced by a still head and the mixture was distilled to a head temperature of 185°. The distillate (ca. 10 mL) was added to cold water, the crude ester was removed from the water layer with a pipette and fractionated to yield 3.5 g (90%) of ethyl 3-methylbutanoate, bp 129–132°. The NMR spectrum was identical to that of the known compound.



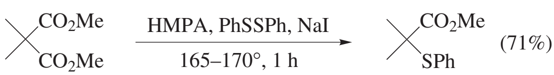
Methyl 6-Oxo-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-9-carboxylate [Dealkoxycarbonylation of a Six-Membered Cyclic Geminal Dimethyl Ester Using Microwave Irradiation].[326] Dimethyl 6-oxo-7,8-dihydropyrido[1,2-*a*]indole-9,9(6*H*)-dicarboxylate (84 mg, 0.28 mmol) was dissolved in DMF (3 mL) in a microwave vial (2–5 mL). LiCl (approximately 2 mg) and water (1 drop) were added and the sealed vial was irradiated in a microwave oven at 180° for 10 min. The cooled mixture was diluted with ether, washed with water, brine, and dried ($MgSO_4$). The solvent was removed under vacuum and the residue was purified by silica gel chromatography (10–40% EtOAc/hexane, gradient elution) to yield the title product (44 mg, 65%) as an orange oil: R_f (EtOAc/hexane 1:1) 0.65; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.27 (dd, J = 8.4, 7.8 Hz, 1H), 7.22 (dd, J = 8.4, 7.8 Hz, 1H), 6.48 (s, 1H), 4.03 (t, J = 6.0 Hz, 1H), 3.73 (s, 3H), 2.98–2.93 (m, 1H), 2.41–2.36 (m, 1H), 2.29–2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 168.3, 135.0, 134.1, 129.2, 124.8, 124.1, 120.2, 116.5, 107.2, 52.6, 39.8, 31.8, 24.1; HRMS (m/z): calcd for $C_{14}H_{13}NO_3$, 243.0895; found, 243.0885.



Ethyl 2,2-Dimethyl-3-(2′,2′-dichlorovinyl)cyclopropane-1-carboxylate [Dealkoxycarbonylation of a Three-Membered Cyclic Geminal Diethyl Ester in 1-Oxo-1-methylphospholine and Recovery of the Solvent].[113] A mixture of 30 g (0.1 mol) of diethyl 2,2-dimethyl-3-(2′,2′-dichlorovinyl)cyclopropane-1,1-dicarboxylate, 6 g (0.1 mol) of NaCl and 4 mL (0.2 mol) of water in 50 mL of 1-oxo-1-methylphospholine was heated at 175° for 9 h. The cooled mixture was poured into 150 mL of water and the product was extracted into petroleum ether. Distillation of the dried ($MgSO_4$) extracts gave 21.3 g (93%) of the title product, bp 65–75° (0.1 mm). No spectral or analytical data were reported. 1-Oxo-1-methylphospholine (49.7 g), bp 75–77° (0.15 mm) was recovered by fractional distillation of the aqueous phase.



Methyl 2-Benzylpent-4-enoate [Dealkoxycarbonylation of an α,α-Disubstituted Dimethyl Malonate in an Ionic Liquid].[115] A mixture of dimethyl 2-allyl-2-benzyl)malonate (131 mg, 0.5 mmol), LiCl (42 mg, 1.0 mmol), and [bmim]Br (0.5 g) was heated at 160° for 14 h, cooled, and poured into water. Extraction with Et_2O, removal of the solvent from the dried solution, and chromatography of the residue (SiO_2) gave 101 mg (99%) of the title product as an oil. No spectral or analytical data were reported.



Methyl 2-Methyl-2-(phenylthio)propanoate [Trapping of an Intermediate Enolate by an Electrophile Other Than a Proton].[226] A mixture of dimethyl α,α-dimethylmalonate (320 mg, 2 mmol), diphenyl disulfide (436 mg, 2 mmol), and sodium iodide (360 mg, 2 mmol) in 2 mL of HMPA was heated at 165–170° for 1 h. The cooled mixture was poured into 50 mL of water and extracted with Et_2O (2 × 50 mL). The extracts were washed with water and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by TLC on silica gel to give 298 mg (71%) of the title product: mp 41–43°; ^1H NMR (CCl_4) δ 7.5–7.1 (m, 5H), 3.55 (s, 3H), 1.4 (s, 6H). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.84; H, 6.71; S, 15.22. Found: C, 62.78; H, 6.63; S, 15.47.

TABULAR SURVEY

The literature was searched through August 2009 using SciFinder, MDL, Crossfire Commander, ISI Web of Knowledge, and Beilstein databases; some later publications were also included. The tables are arranged according to substrates; their titles are listed in the Table of Contents. α-Acyl derivatives of malonic esters, β-keto esters, and α-cyano esters are listed separately (Tables 5, 10, and 14, respectively) rather than in the tables dealing with the respective monosubstituted derivatives. Substrates where the reacting ester group is attached to a ring are collected in separate tables according to ring size; the smallest ring determines the location in bicyclic derivatives. Within each table substrates are arranged by increasing carbon-count. In order to group similar substrates together, protecting groups, chiral auxiliaries, and simple groups on heteroatoms (N, O, P, S, Se, Si) are not included in the carbon-count. Within each carbon-count, entries are arranged loosely in the order of saturated chains, chains containing unsaturation, cyclic derivatives in increasing ring size, aromatic substrates, and finally substrates containing heterocyclic rings in the order of N, O, and S.

An em-dash enclosed in parentheses [(—)] next to a product signifies that it was isolated but no yield was reported. In sub-tables, the stereochemical designations of starting materials are listed before the yield, those of products are given after the yield. In cases where the dealkoxycarbonylation of a substrate has been reported using identical or very similar conditions in more than one publication, the conditions producing the highest yield are reported and the reference to that paper is given first.

The following abbreviations are used in the tables. Only those not in the *Journal of Organic Chemistry* List of Standard Abbreviations and Acronyms are given here.

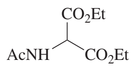
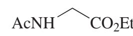
Alloc	allyloxycarbonyl
[bmim]	*N*-butyl-*N*′-methylimidazolium
BOM	benzyloxymethyl
DHP	dihydropyranyl
DMB	2,4-dimethoxybenzyl
DMEU	*N*,*N*′-dimethyl-*N*,*N*′-ethyleneurea
Krapcho	no conditions are reported but reference is made to the ones in Krapcho, A. P. *Synthesis* **1982**, 805 and Krapcho, A. P. *Synthesis* **1982**, 893. Standard conditions are heating in wet DMSO in the presence of a salt (LiCl, NaCl, or NaCN) until carbon dioxide evolution ceases.
MS	molecular sieves
Mw	microwave irradiation
PATP	4-aminothiophenol
PhthN	phthalimido
PMP	4-methoxyphenyl
PNB	4-nitrobenzyl
PNP	4-nitrophenyl
TBDPS	*tert*-butyldiphenylsilyl
TES	triethylsilyl
TMAA	tetramethylammonium acetate
Triton B	benzyltrimethylammonium hydroxide
12-c-4	1,4,7,10-tetraoxacyclododecane
18-c-6	1,4,7,10,13,16-hexaoxacyclooctadecane

TABLE 1. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED MALONATES

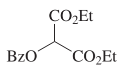
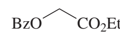
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
CO_2Me CO_2Me	$(n\text{-}Bu)_4NI$, heat	$MeCO_2Me$ (35)	327
CO_2Et CO_2Et	DMSO, Triton B, 80°, 4 h	$MeCO_2Et$ (75)	328
	B_2O_3, 150°	MeCOMe[a] (84)	329
CO_2Et CO_2t-Bu	DMSO, H_2O, reflux, 4 h	$MeCO_2Et$ **I** + $MeCO_2t$-Bu **II** **I** + **II** (—), **I**/**II** = 10:1	18
	DMSO, H_2O, LiCl, reflux, 4 h	**I** + **II** (—), **I**/**II** = 6:1	18
CO_2t-Bu CO_2t-Bu	DMSO, H_2O, reflux, 4 h	$MeCO_2t$-Bu (—) + t-BuOH (—)	18

[a] The product was formed by a sequence including a Claisen condensation.

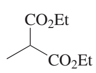
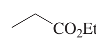
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	See table.		

Solvent(s)	Additive(s)	Temp	Time (h)		Refs.
dioxane, EtOH	KOH, 18-c-6	rt; then reflux	1; 20	(80)	330
DMSO	H_2O	reflux	3.5	(70)	15

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	See table.	 **I** + BzOEt **II** + BzOH **III**	331

Solvent	Additive(s)	Temp (°)	Time (h)	I	II	III
DMSO	—	200	4	(50)	(0)	(0)
DMSO	H_2O, Na_3PO_4	200	4	(40)	(11)	(0)
DMSO	H_2O, LiCl	200	4	(7)	(6)	(0)
DMSO	H_2O, NaCl	200	4	(22)	(27)	(0)
DMSO	H_2O, NaBr	200	4	(13)	(2)	(0)
DMSO	NaCN	—	—	(0)	(42)	(0)
pyridine	LiI	reflux	12	(47)	(0)	(29)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	DMSO, additive(s)		

Additive(s)	Temp (°)	Time (h)		Refs.
—	reflux	11	(5)	332
H_2O	167	3	(32)	332
H_2O	reflux	15	(80)	15
H_2O, NaCl	reflux	2	(56)	332
NaCN	160	4	(75)	108
Triton B	80	4	(79)	328

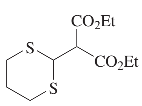
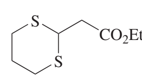
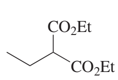
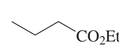
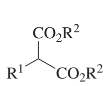
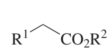
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, reflux, 45 min	 (95)	243

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	See table.		

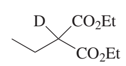
Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
DMSO	H_2O	190	3	(19)	332, 15
DMSO	H_2O, LiCl	reflux	4	(99)	15
DMSO	H_2O, NaCl	190	3	(74)	332
DMSO	H_2O, NaCl	165	4	(90)	333
DMSO	NaCN	160	4	(80)	108
DMSO	H_2O, KCN	reflux	1.5	(94)	15
DMSO	Triton B	80	48	(81)	328
DMA	H_2O	reflux	17	(30)	332
n-$C_7H_{15}CO_2H$	$(n\text{-Bu})_4PCl$	200	6	(79)	321
o-xylene	DABCO	reflux	24	(33)	291

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{5–25}$ 	See table.		

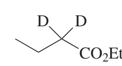
R^1	R^2	Solvent	Additive(s)	Temp (°)	Time		Refs.
$BnO(CH_2)_2$	Et	DMSO	H_2O, LiCl	170	5 h	(95)	334
n-Pr	Et	PhH, EtOH	KOH, 18-c-6	rt; then reflux	1 h; 14 h	(59)	330
i-Pr	Et	DMSO	H_2O	reflux	2 h	(1)	15
i-Pr	Et	DMSO	H_2O, LiCl	reflux	4 h	(96)	15
c-Pr	Et	DMSO	NaCN	160	4 h	(52)	335
n-Bu	Et	DMSO	H_2O, LiCl	reflux	3 h	(95)	15
n-Bu	Et	—	B_2O_3	170–190	4 h	(94)	311
n-Bu	Et	PhH, EtOH	KOH, 18-c-6	rt; then reflux	1 h; 23 h	(84)	330
i-Bu	Et	DMSO	H_2O	reflux	2 h	(13)	15
i-Bu	Et	DMSO	H_2O, LiCl	reflux	4 h	(99)	15
$MeCH(CD_3)CH_2$	Et	DMSO	H_2O, NaCl	155	—	(75)	336

$F(CH_2)_2CHMe$	Et	DMSO	NaCN	160	4 h	(16)	337
n-C_5H_{11}	Et	—	B_2O_3	170–190	4 h	(94)	311
$EtCHMeCH_2$	Me	DMSO	H_2O, LiCl	180	15 h	(79)	338
i-$Pr(CH_2)_2$	Et	Krapcho	—	—	—	(—)	339
i-$Pr(CH_2)_3$	Me	DMSO	H_2O	reflux	1 h	(10)	20
i-$Pr(CH_2)_3$	Me	DMSO	H_2O, LiCl	reflux	1 h	(99)	20
i-$Pr(CH_2)_3$	Me	DMSO	H_2O, NaCl[a]	reflux	1 h	(99)	20
i-$Pr(CH_2)_3$	Et	DMSO	H_2O	reflux	1 h	(2)	20
i-$Pr(CH_2)_3$	Et	DMSO	H_2O, LiCl[b]	reflux	2 h	(99)	20
c-C_6H_{11}	Et	DMSO	H_2O	reflux	2 h	(1)	15
c-C_6H_{11}	Et	DMSO	H_2O, NaCl	reflux	4 h	(99)	15
n-$C_{10}H_{21}$[c]	Et	H_2O	LiBr, Aliquat 336	Mw, 200	10 min	(60)[d]	340
n-$C_{16}H_{33}$	Et	DMSO	H_2O, NaCl	158–170	5 h	(90–95)	333
n-$C_{18}H_{37}$[c]	Et	H_2O	LiBr, Aliquat 336	Mw, 200	10 min	(57)[d]	340
n-$C_{18}H_{37}$	Et	o-xylene	DABCO	reflux	10.5 h	(77)	291
n-$C_{18}H_{37}$	Et	o-xylene	3-quinuclidinol	reflux	7 h	(96)	291
n-$C_{22}H_{45}$	Et	DMSO	H_2O, NaCl	154–170	6 h	(90–95)	333

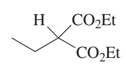
C_5



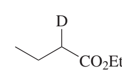
DMSO, D_2O, reflux, 4 h



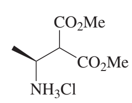
(70) 90% D incorporation — 264



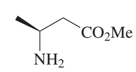
DMSO, D_2O, reflux, 4 h



(60) — 264



DMSO, H_2O, NaCl, reflux, 2 h

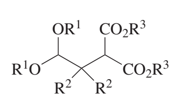


(85) 97.5:2.5 er — 76

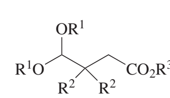
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

$C_{5–7}$

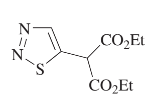


DMF, additive(s), reflux

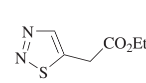


R^1	R^2	R^3	Additive(s)	Time (h)		Refs.
Me	H	Me	LiCl	2	(74)	341
Et	H	Et	H_2O, NaCl	72	(68)	342
Me	Me	Me	LiCl	2	(83)	341

C_5

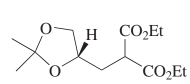


H_2O, LiBr, Me_4NBr, Mw (120W), 30 min

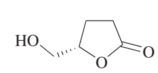


(87) — 343

C_6

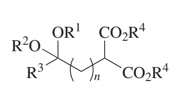


DMA, H_2O, $MgCl_2$•$6H_2O$, reflux, 20 h

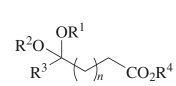


(95) — 344, 345

$C_{6–9}$

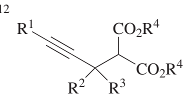


See table.

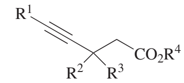


n	R^1	R^2	R^3	R^4	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
2	Me	Me	H	Me	DMF	H_2O, NaCl	reflux	35	(69)	275
2	—$(CH_2)_2$—		H	Et	DMSO	H_2O, LiCl	reflux	3	(70)	346, 347
2	—$(CH_2)_2$—		H	Et	DMSO	NaCN	160–170	4	(50)	348
2	—$(CH_2)_2$—		H	Et	DMSO	NaCl	180	—	(—)	349
2	—$(CH_2)_2$—		Me	Et	DMSO	NaCN	160	5	(63)	350
4	—$(CH_2)_2$—		Me	Et	DMSO	H_2O, NaCl	160	4	(61)	351

C_{6-12}

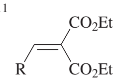


See table.

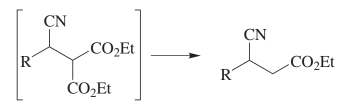


R^1	R^2	R^3	R^4	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
H	H	H	Et	DMSO	LiCl	reflux	—	—	352, 353
H	Me	Me	Et	DMSO	H_2O, NaCl	180	19	(82)	354, 355, 113
H	Me	Me	Et	DMSO	NaBr	190	20	(88)	114
H	Me	Me	Et	1-oxo-1-ethylphospholine	H_2O, Et_4NCl	180	12	(75)	113
H	*i*-Pr	H	Me	DMF	H_2O, LiCl	150	1.5	(85)	356, 357
Et	H	H	Et	DMSO	H_2O, NaCl	160	8	(65)	358
n-Bu	H	H	Et	DMSO	H_2O, NaCl	180	—	(60)	359
Ph	H	H	Et	DMSO	H_2O, LiCl	—	—	(69)	352, 360
n-C_6H_{13}	H	H	Et	DMSO	H_2O, NaCl	170–180	8	(60)	361

C_{6-11}

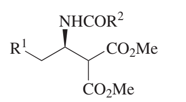


EtOH, H_2O, KCN

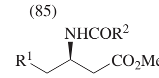


R	Temp (º)	Time (h)		Refs.
Me	60	7	(71)	362, 363
Ph	65–75	18	(85)	364, 365

C_6



DMSO, H_2O

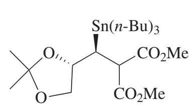


R^1	R^2	er	Temp (º)	Time (h)		er	Refs.
Me	CF_3	91.5:8.5	160	18	(69)	—	79
t-BuSCO	Ph	—	150	20	(65)	—	77

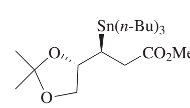
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

C_6

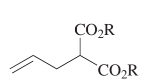


See table.



122

Solvent	Additive(s)	Temp (º)	Time (h)	
DMSO	NaCl	160	24	(0)
HMPA	$Me_4N^+AcO^-$	100	1.5	(53)
DMF	PATP, Cs_2CO_3	90	5.5	(55)



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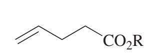
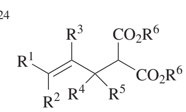


R	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
Me	—	H_3BO_3	170–190	4	(95)	311, 366
Et	DMSO	H_2O, NaCl	160–180	8	(82)	315, 368
Et	PhH, EtOH	KOH, 18-c-6	rt; then reflux	—; 24	(79)	330
Et	*n*-$C_{17}H_{35}CO_2H$	$(n\text{-Bu})_4PCl$	200	4	(69)	321

C_{6-24}



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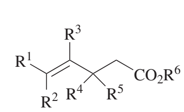
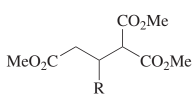


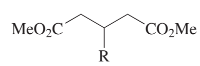
R^1	R^2	R^3	R^4	R^5	R^6	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
H	H	Br	H	H	Et	DMSO	H_2O, NaCl	reflux	8	(67)	369
H	Me	H	H	H	Et	DMSO	H_2O, NaCl	180	—	(90)	370, 371
H	H	Me	H	H	Me	DMSO	H_2O, NaCl	150	12	(74)	373
H	H	H	Me	Me	Me	DMSO	H_2O, NaCN	160	—	(60)	372
H	H	$AcO(CH_2)_2$	H	H	Me	DMSO	H_2O, NaCl	150	5	(79)	374
H	*n*-C_5H_{11}	H	H	H	Et	DMSO	H_2O, NaCl	140–145	8	(80)	375

H	n-C_6H_{13}	H	H	H	Et	DMSO	H_2O, NaCl	140–145	8	(78)	376
Me	H	H	H	H	Et	DMSO	H_2O, NaCl	180	—	(69)	370, 371
Me	H	H	Me	H	Me	DMF	LiI, NaCN	130	—	(80)	377
Me	Me	H	H	H	Me	Krapcho	—	—	—	(49)[d]	378
Me	Me	H	H	H	Et	DMSO	H_2O, LiCl	reflux	5	(95)	379, 380
Me	Me	H	H	H	Et	DMSO	H_2O, NaCl	reflux	20	(80)	381, 335, 382, 367
Me	Me	H	H	H	Et	DMSO	H_2O, NaCN	160	4	(59)	383
Me	Me	Me	H	H	Me	DMSO	H_2O, NaCl	170	4.5	(—)	384
Me	Et	H	H	H	Et	DMSO	H_2O, NaCl	—	—	"good"	385
Me	Me	H	Me	Me	Et	DMSO	H_2O, NaCN	160	4	(70)	386
Et	Me	H	H	H	Et	DMSO	H_2O, NaCl	—	—	"good"	385
n-Pr	H	H	H	H	Me	DMSO	H_2O, NaCl	155	3.25	(82)	387
$Me_2C(OH)$	H	H	Me	Me	Me	DMSO	—	—	—	(—)	388
n-C_5H_{11}	Et	H	H	Me	Et	DMSO	H_2O, NaCl	—	—	(76)	389
Ph	H	H	H	H	Et	DMSO	H_2O, NaCl	180	6	(75)	390
Ph	H	H	H	Ph (R)	Me	DMSO	H_2O, NaCl	170	13	(80)	391
Ph	Ph	H	H	ClC_6H_4 (S)	Me	Krapcho	—	—	—	(—)	392

$C_{6–12}$



See table.



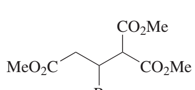
Continued on next page.

R	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
H	Krapcho	—	—	—	(—)	393
$PhMe_2Si$	DMSO	H_2O, NaCl	160	2.5	(97)[d]	394
$PhMe_2Si$	DMSO	H_2O, NaCl	130	48	(89)	395
4-$MeC_6H_4Me_2Si$	DMSO	H_2O, NaCl	130	48	(89)	395
Me	DMSO	H_2O, NaCl	reflux	4.5	(93)	396
$BnOCH_2$	Krapcho	—	—	—	(—)	393

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

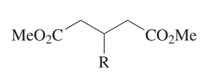
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

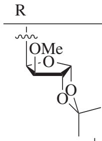
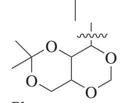
$C_{6–12}$



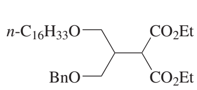
Continued from previous page.

See table.

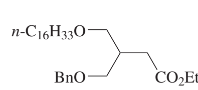


R	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
	Krapcho	—	—	—	(—)	393
	Krapcho	—	—	—	(—)	393
Ph	Krapcho	—	—	—	(—)	393

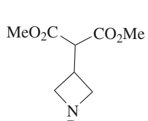
C_6



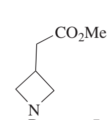
DMSO, additive(s)



Additive(s)	Temp (°)		Refs.
H_2O, NaCl	—	(<79)	397
$(n\text{-}Bu)_4N^+AcO^-$	130	(79)	



DMSO, H_2O, additive



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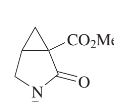
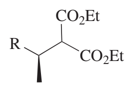


II

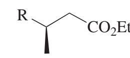
398

Additive	Temp (°)	Time (h)	I	II
NaCl	150	2	(0)	(30)
NaCN	110	6	(49)	(0)

C_{7-13}



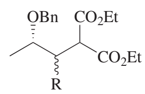
DMSO or DMF, H_2O, LiCl, 160°, 8–12 h



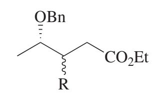
R		Config.
Et	"excellent"	(*S*)
n-Pr	(—)	(*S*)
i-Pr	(—)	(*R*)
i-Bu	(—)	(*S*)
2-furyl	(—)	(*R*)
$Ph(CH_2)_2$	(—)	(*S*)

399

C_{7-10}



DMSO, H_2O, NaCl

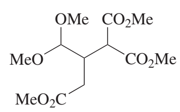


(—)

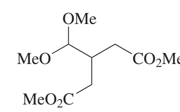
R	Config.
Me	*anti*
Me	*syn*, (2*S*,3*S*)
n-Bu	*anti*
n-Bu	*syn*, (2*S*,3*S*)

400

C_7

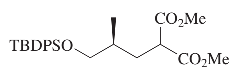


DMSO, H_2O, NaCl, 160°



(75)

401



DMSO, H_2O, NaCl, 160°, 4 h

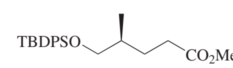


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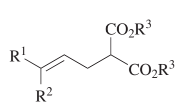
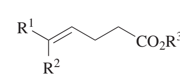
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

C_7

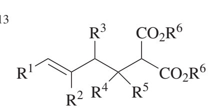


DMSO, additive(s)

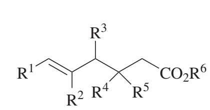


R^1	R^2	R^3	Additive(s)	Temp (°)	Time (h)		Refs.
H	$THPOCH_2$	Me	H_2O, NaCN	140–145	5	(53)	403
H	$THPOCH_2$	Me	KOAc	140	5	(81)	404, 405
H	$THPOCH_2$	Et	NaCN	160	4	(64)	406, 407
$HOCH_2$	H	Me	H_2O, NaCl, 2,6-di-*tert*-butyl-4-methylphenol	150	15	(84)	408
$THPOCH_2$	H	Me	KOAc	140	—	(88)	409
$THPOCH_2$	H	Me	H_2O, NaCN	140–145	5	(48)	403

C_{7-13}

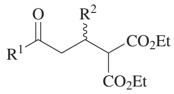


See table.

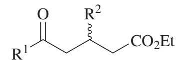


R^1	R^2	R^3	R^4	R^5	R^6	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
H	H	H	H	H	Et	DMSO	LiCl	—	—	(85)	410
H	H	H	H	H	Et	DMSO	H_2O, NaCl	150	48	(82)	411
H	H	H	H	H	Et	Krapcho	—	—	—	(76)	412, 413
H	Me	H	H	H	Me	Krapcho	—	—	—	(62)	378
H	H	H	Me	H	Et	DMSO	H_2O, LiCl	"heat"	14	(84)	416
H	H	Me	Me	H	Me	DMSO	H_2O, NaCl	—	—	(—)	414
H	H	Me	Me	H	Et	HMPA	$Me_4N^+AcO^-$	110	10	(90)	415
H	H	H	Me	Me	Et	DMSO	H_2O, LiCl	reflux	14	(82–86)	417, 416, 418
H	H	H	Me	Me	Et	DMSO	H_2O	—	—	(60)	419
H	H	H	Me	Me	*i*-Pr	DMSO	H_2O, LiCl	—	—	$(20)^d$	418
Ph	H	H	H	H	Et	DMSO	H_2O, NaCl	180	6	(—)	390

C_{7-15}

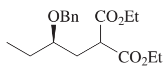


DMSO, H_2O, NaCl

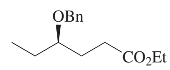


R^1	R^2	Config.	Temp (°)	Time (h)		er	Refs.
Me	H	(*R*,*S*)	148	8	(80)	—	420
Me	$PhMe_2Si$	(*R*,*S*)	170	4	(82)	—	421
n-C_9H_{19}	$PhMe_2Si$	(*S*)	85	48	(85)	95.0:5.0	422

C_7



DMSO, H_2O, LiCl, 140°, 48 h



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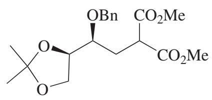
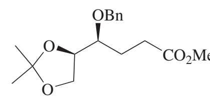


DMSO, H_2O, NaCl, 190°



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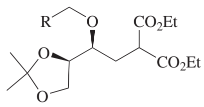

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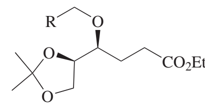

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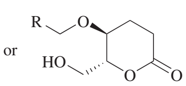
or



II

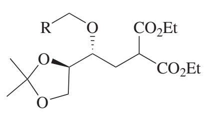
424

R	Solvent	Additive	Temp	Time (h)	I	II
Ph	DMSO	NaCl	reflux	2	(91)	(0)
Ph	DMA	$MgCl_2•6H_2O$	reflux	22	(0)	(64)
n-$C_{15}H_{31}$	DMA	$MgCl_2•6H_2O$	reflux	22	(0)	(60)

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

C_7



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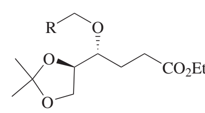

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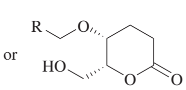
or

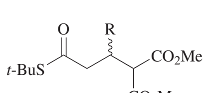


II

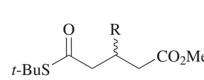
424

R	Solvent	Additive	Temp	Time (h)	I	II
Ph	DMSO	NaCl	reflux	2	(80)	(0)
n-$C_{15}H_{31}$	DMA	$MgCl_2•6H_2O$	reflux	22	(0)	(60)

C_{7-12}



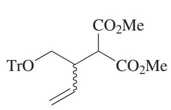
DMSO, H_2O, NaCl, 130°



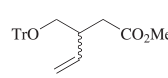
R	Config.	Time (h)	
Me	(*R*)	40	(69)
i-Pr	(*S*)	40	(67)
c-C_6H_{11}	(*S*)	24	(81)
Ph	(*S*)	24	(86)

425, 426

C_7

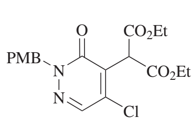


DMSO, H_2O, NaCl, 160°, 22 h

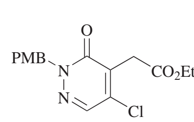


Config.		er
(*S*)	(—)	99.5:0.5
(*R*)	(—)	—

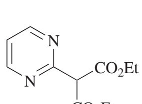
427



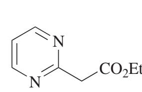
DMSO, H_2O, LiCl, 135°, 2 h



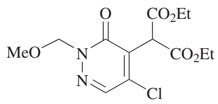
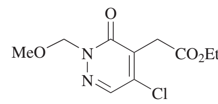
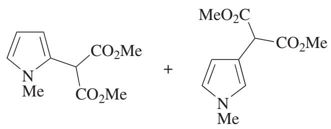
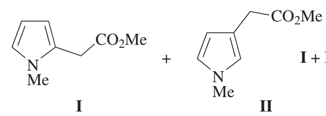
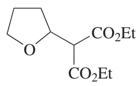
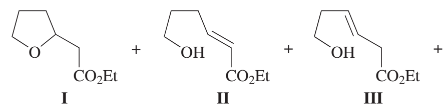
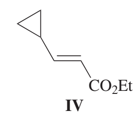
(99) 428



DMSO, H_2O, 180°, 20 min



(62) 429

	DMSO, H_2O, NaCl, 170°, 16 h	 (48)	430
	DMF, H_2O, LiCl, reflux, 1 h	 **I** + **II** (47), **I**/**II** = 6.5:1	431
	DMSO, additive(s), reflux	 +  **IV**	243

Additive(s)	Time (h)	I	II	III	IV
NaCl	—	(30)	(0)	(0)	(15)
H_2O, NaCl	1.5	(19)	(23)	(34)	(0)

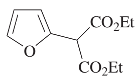
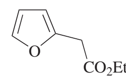
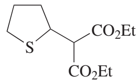
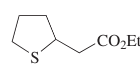
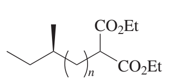
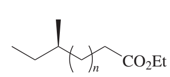
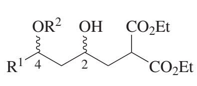
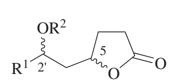
	NMP, HOAc, LiCl, reflux, 5 h	 (86)	432
	DMSO, H_2O, NaCl, reflux, 3 h	 (80)	243

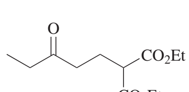
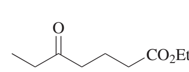
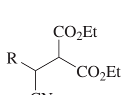
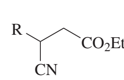
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-10}			
	DMSO, H_2O, additive		

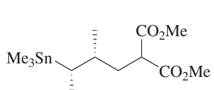
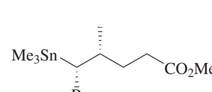
n	Additive	Temp (°)	Time (h)		Refs.
1	LiCl	reflux	4	(78)	433
3	NaCl	155	48	(89)[e]	434

	DMF, $MgCl_2$•$6H_2O$, reflux		

R^1	R^2	Config.		Config.	Refs.
Me	Bn	racemic	(70)[d]	racemic	168
Me	TBDPS	racemic	(95)[d]	racemic	
n-Pr	TBDPS	(2*S*,4*S*)	(73)[d]	(2'*S*,5*S*)	

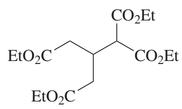
C_8			
	DMSO, H_2O, NaCl, 160°, 6 h	 (75)	435
C_{8-9}			
	DMSO, H_2O, NaCl		

R	Temp (°)	Time (h)		Refs.
i-Pr	140–148	9–10	(94)	436
i-Bu	137–148	8.5	(86)	437

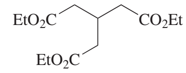
C_{8-13}			
	DMSO, H_2O, LiCl, reflux, 10 min		438

R	
Me	(77)
Ph	(75)

C_8

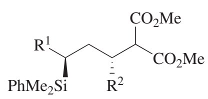


DMSO, H_2O, NaCl



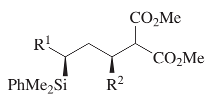
(—) 439

$C_{8–18}$



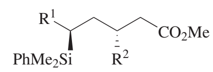
I

+



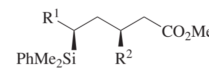
II

DMSO, H_2O, LiCl, reflux, 30 min



III

+



IV

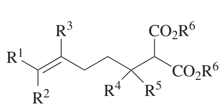
440

R^1	R^2	**I/II**	**III + IV**	**III/IV**
Me	Me	85:15	(81)	85:15
Me	Ph	29:71	(52)	29:71
i-Pr	Me	64:36	(68)	64:36
i-Pr	Me	52:48	(60)	52:48
i-Pr	Ph	37:63	(—)	37:63
Ph	Me	81:19	(71)	84:16
Ph	Ph	100:0	(71)	100:0

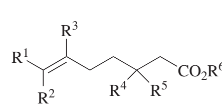
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

$C_{8–11}$

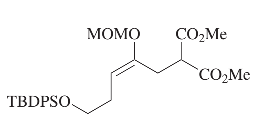


See table.

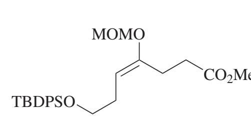


R^1	R^2	R^3	R^4	R^5	R^6	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
H	H	H	H	H	Et[f]	DMSO	H_2O, NaCl	reflux	4	(68)	441
H	H	Me	H	H	Et	DMSO	H_2O, LiCl	150–180	10–12	(67)	135
H	H	Me	H	H	*i*-Pr	DMSO	H_2O, LiCl	150–180	10–12	(60)	135
H	H	H	Me	Me	Et	DMSO	H_2O, LiCl	reflux	—	(55)	417
Me	Me	H	Me	H	Et	DMSO	H_2O, LiCl	180	8	(87)	442
Me	Me	H	Me	H	Et	DMF	LiI	150	4	(71)	443
Et	H	H	H	H	Et	DMSO	H_2O, NaCl	130	8	(80)	444
i-Pr	H	H	H	H	Et	DMSO	H_2O, NaCl	185	5	(65)	445

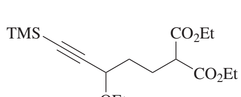
C_8



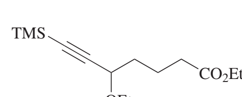
DMSO, NaCN, 90°, 64 h



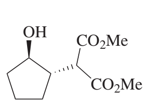
(67) 446



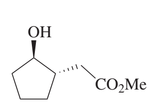
DMSO, H_2O, NaCl, 150°, 15 h



(55) 447

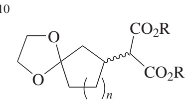


DMSO, H_2O, LiCl, 140°, 3 h

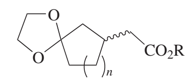


(82) 170

C_{8-10}

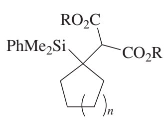


See table.

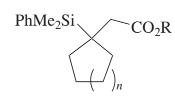


n	R	Config.	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
1	Me	(*R*)	DMSO	H_2O, LiCl	—	—	(76)	449–451
1	Et	(*S*)	DMSO	H_2O, LiCl	180	4	(84)	452
2	Me	(*R*,*S*)	DMSO	H_2O, LiCl	140	17	(59)	453
2	Me	(*R*)	DMSO	H_2O, LiCl	—	—	(88)	449–451
2	Me	(*R*)	DMSO	H_2O, LiCl	140	17	(97)[d]	454–456
2	Me	(*S*)	PhMe	H_2O, DABCO	reflux	4	(66)	457
2	Me	(*S*)	DMSO	LiI•$2H_2O$	"heat"	—	(82)[g]	458
2	Et	(*R*,*S*)	DMSO	H_2O, NaCl	165	18	(96)	459
2	Et	(*R*,*S*)	DMSO	NaCN	155	16	(73)	460

C_{8-9}



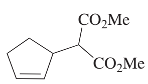
DMSO, H_2O, LiCl, reflux, 45 min



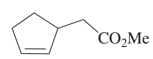
n	R	
1	Et	(75)
2	Me	(90)

461

C_8



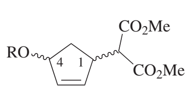
DMSO, H_2O, NaCN



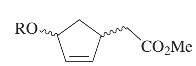
(70–90) 462

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

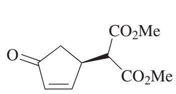
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.



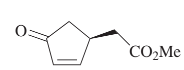
Additive(s), 130º



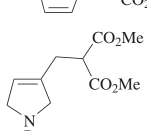
R	Config.	Solvent	Additive(s)	Time (h)		Refs.
H	(1*R*,4*S*)	DMEU	H_2O, KI	10	(—)	463, 464, 465
TBS	(1*R*,4*S*)	DMEU	H_2O, KI	10	(89)	463, 464, 465
TBS	(1*R*,4*S*)	DMF	LiI	17	(75)	466
Tr	(1*R*,4*R*)	DMF	LiI	17	(63)	466
Tr	(1*S*,4*R*)	DMF	LiI	17	(80)	466
TBS	(1*S*,4*S*)	DMF	LiI	17	(74)	466



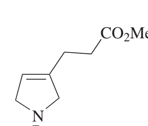
—



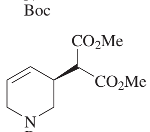
(—) 467, 468



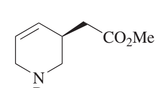
DMF, H_2O, NaCl, 150°, 30 min



(92) 469



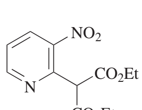
DMSO, H_2O, NaCl, 5.5 h



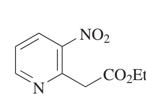
R	Temp (º)	
Boc	reflux	(90)
Cbz	100	(70)

137

C_8



DMSO, H_2O, LiCl, 100°, 12 h; then LiCl, 100°, 5 h



(92) 470, 471, 472

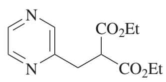
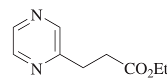
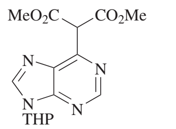
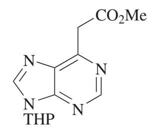
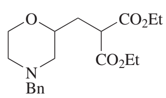
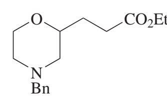
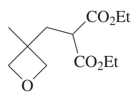
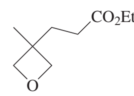
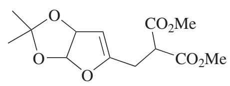
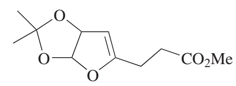
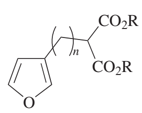
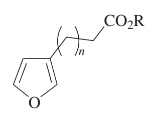
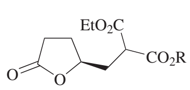
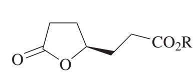
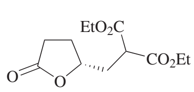
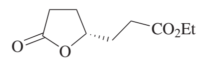
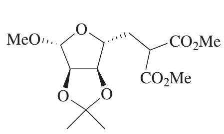
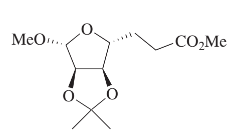
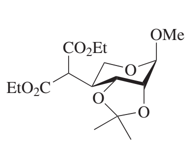
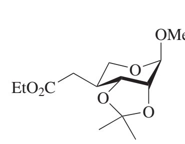
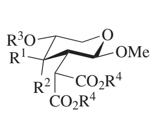
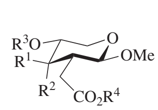
	DMSO, H_2O, NaCl, 155–170°, 6 h	 (77)	473
	—	 (0)	474
	DMF, H_2O, NaCl, reflux, 24 h	 (98)	475
	DMSO, H_2O, NaCl, 110°, 5 h	 (71)	476
	Krapcho	 (—)	477
C_{8-11}			
	DMSO, H_2O, NaCl	 *n* / R / Temp (°) / Time (h) 1 / Et / 160 / 4 / (79) 4 / Me / reflux / 3 / (90)	478, 479 480

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	DMSO, H_2O, NaCl, 175–180°	 R / Time (h) Et / 6–7 / (99) Bn / 10 / (92)	82
	DMSO, H_2O, NaCl, 175–180°, 6–7 h	 (—)	82
	DMSO, H_2O, NaCl, 160°, 3 h	 (84)[d]	481
	DMSO, H_2O, LiCl, reflux, 4 h	 (100)	482
	A. DMSO, LiI, 180°, 5–7 h B. DMSO, LiI, 10 bar, Mw (200 W), 100°, 10–20 min	 R^1 / R^2 / R^3 / R^4 / Cond. H / AcO / Ac / Me / A / (79) H / AcO / Ac / *i*-Pr / A / (81) H / BnO / Bn / Me / B / (83) AcO / H / Ac / Me / A / (81) AcO / H / Ac / *i*-Pr / A / (82) BnO / H / Bn / Me / B / (83)	89, 483

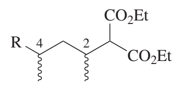
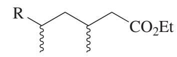
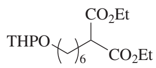
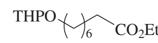
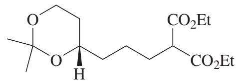
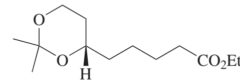
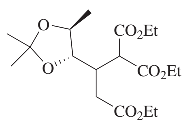
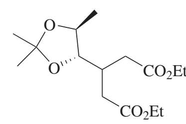
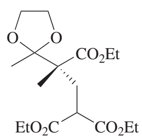
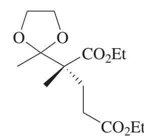
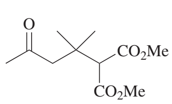
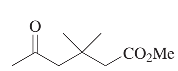
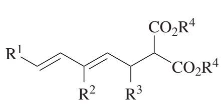
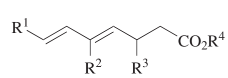
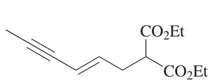
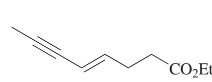
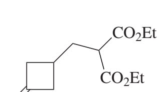
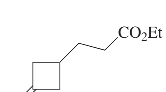
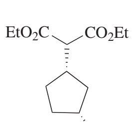
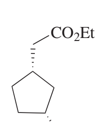
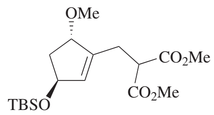
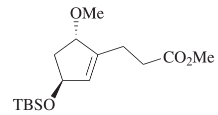
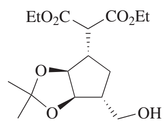
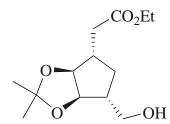
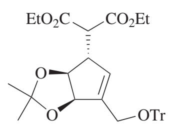
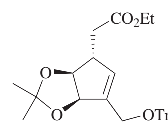
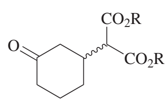
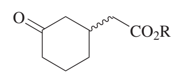
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10}			
	DMSO, H_2O, LiCl	 R: Me, Config. (2*S*) (—); R: Et, Config. (2*R*,4*S*) (62)[d]; R: Et, Config. (2*S*,4*S*) (80)[d]	399
C_9			
	DMSO, additive(s)	 Additive(s): H_2O, NaCl; Temp (°): 160; Time (h): 4 (66)	245
		Additive(s): KOAc; Temp (°): 80; Time (h): 6 (92)	119
	DMSO, NaCN, 175–180°, 3.5 h	 (43)[d]	484
	DMSO, H_2O, NaCl	 Temp: 160°; Time: 3 h (0); Temp: Mw (800 W); Time: 15 min (58)	131
	DMSO, H_2O, NaCN, 160°, 6 h	 (72)	485

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	DMSO, H_2O, NaCl	 (—)	486
C_{9-12}			
	See table.		

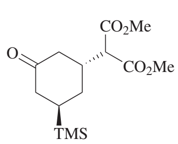
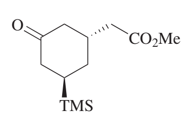
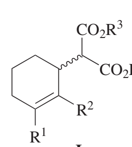
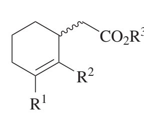
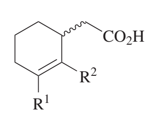
R^1	R^2	R^3	R^4	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
H	Me	H	Me	DMSO	NaCN, H_2O	80	36	(88)	487
Me	H	H	Me	DMSO	NaCN	120	3	(75)	488
Me	H	H	Et	DMF	LiI	150	4	(60)	489
Me	H	*n*-Pr	Et	DMF	LiI	150	4	(93)	489

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	DMSO, NaCN, 120°, 3 h	 (100)	448
	DMSO, H_2O, NaCl, 140°	 (65)	490
	DMSO, H_2O, LiCl, 178°, 4.25 h	 (69)	171

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhH, MeOH, KOH, 18-c-6, rt, 8 h; then reflux, 1 h	 (83)	491
	DMSO, H_2O, LiCl, 180°	 (—)	171
	DMSO, H_2O, LiCl, 175°, 3 h	 (86)	324
	See table.		

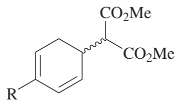
R	Config.	er	Solvent	Additive(s)	Temp	Time		er	
Me	(*R*)	91.5:8.5	DMSO	H_2O, LiI	170º	1 h	(34)	89.5:10.5	74
Me	(*R*)	99.5:0.5	DMSO	LiI•3H_2O	180º	25 min	(52)	>99.5:0.5	73
Me	(*R*)	99.5:0.5	DMSO	H_2O, LiCl	160º	16 h	(78)	>95.0:5.0	492
Me	(*R,S*)	—	DMSO	LiI•3H_2O	reflux	—	(73)	—	493
Me	(*R,S*)	—	Krapcho	—	Mw	—	(—)	—	494
Et	(*R*)	96.5:3.5	DMSO	H_2O	175º	3 h	(0)	—	74
Et	(*R*)	96.5:3.5	DMSO	H_2O, NaCl	175º	3 h	(36)	93.0:7.0	74
Et	(*R*)	96.5:3.5	DMSO	H_2O, LiCl	170º	3 h	(42)	68.5:31.5	74
Et	(*R*)	96.5:3.5	neat	H_2O (2 eq), LiBr, (*n*-Bu)$_4$NBr	Mw (30 W)	10 min	(84)	88.0:12.0	74
Et	(*R*)	96.5:3.5	neat	H_2O (2 eq), LiBr, (*n*-Bu)$_4$NBr	175º	5 h	(46)	72.0:28.0	74

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

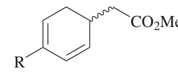
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	Krapcho	 (—)	495
 **I**	DMSO, additive(s)	 **II** +  **III**	

R^1	R^2	R^3	Config.	**I** er	Additive(s)	Temp (º)	Time (h)	**II**	**III**	**III** er	
H	H	Me	(*R,S*)	—	LiI•3H_2O	180	1.5	(85)	(0)	—	496, 166
H	H	Me	(*R,S*)	—	H_2O, NaCl	reflux	1.5	(94)	(0)	—	165
H	H	Me	(*R,S*)	—	H_2O, NaCN	—	—	(70–90)	(0)	—	462
H	H	Me	(*R*)	—	H_2O, NaCl	160	24	(74)	(0)	—	497
H	H	Me	(*R*)	97.0:3.0	H_2O, NaCN	reflux	overnight	(0)	(94)	91.0:9.0	164
H	H	Me	(*S*)	98.0:2.0	H_2O, NaCl	160	—	(—)	(0)	—	498
H	H	Me	(*S*)	—	H_2O, NaCN	160	—	"good"	(0)	—	164
H	H	Me	(*S*)	99.5:0.5	H_2O, NaCN	reflux	overnight	(0)	(99)	93.0:7.0	164
H	H	Et	(*R,S*)	—	H_2O, LiCl	190	6	(84)	(0)	—	499, 500
H	H	Et	(*R,S*)	—	H_2O, NaCl	170	10	(88)	(0)	—	501
H	Br	Et	(*R,S*)	—	H_2O, NaCl	170	5	(78)	(0)	—	502
H	Me	Et	(*R,S*)	—	H_2O, NaCl	160	15	(70)	(0)	—	503
Me	H	Me	(*R,S*)	—	LiI•3H_2O	180	1.5	(80)	(0)	—	504

C$_{9-10}$

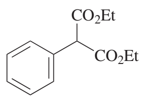


DMSO, H_2O, NaCN

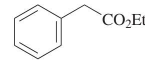


R	Config.	Temp (°)	Time (h)		Refs.
H	(*R,S*)	75	30	(91)	505, 506[h]
H	(*S*)	110	24	(62)	507
H	(*R*)	—	—	(—)	508
Me	(*S*)	60	48	(80)	509, 507

C$_9$

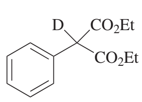
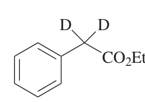
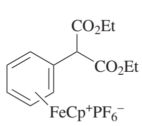
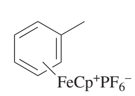
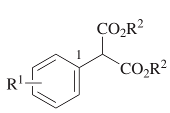
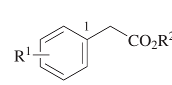


See table.



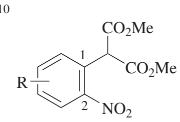
Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
DMSO	H_2O	146–155	3	(93–96)	116, 332, 15
DMSO	H_2O, NaCl	135–170	2	(90–95)	333
DMSO	Triton B	50	6	(77)	328
DME	K_2CO_3	120	67	(62)	510
DME	Cs_2CO_3	120	70	(83)	510
PhH, EtOH	KOH, 18-c-6	rt; then reflux	20; 1	(78)	330
o-xylene	DBN	reflux	0.5	(59)	882
—	B_2O_3	170–190	4	(90)	311

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

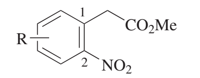
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_9$ 	DMSO, D_2O, reflux, 4 h	 (80)	264
	DMSO, H_2O, NaCl, 160°, 5 h	 (—)	147
C$_{9-12}$ 	See table.		

R^1	R^2	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
H	Me	Krapcho	—	—	—	(—)	511
3-F, 5-BnO	Et	DMSO	H_2O, LiCl	reflux	5	(57)	512
2-I, 4-O_2N, 5-BocNH	Me	DMSO	H_2O, LiCl	100	7	(47)	512a
Cl[j]	Me	Krapcho	—	—	—	(—)	511
2-O_2N	Me	H_2O	K_2CO_3	60	—	(70)	513
2,6-$(O_2N)_2$	Me	Krapcho	—	—	—	(—)	514
MeO[i]	Me	Krapcho	—	—	—	(—)	511
2-O_2N, 4-CF_3	Me	DMSO	H_2O, NaCl	120	2	(80)	515
Me[j]	Me	Krapcho	—	—	—	(—)	511
2,4,6-Me_3	Me	Krapcho	—	—	—	(—)	511

C$_{9-10}$

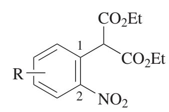


DMSO, H_2O, LiCl, 100°

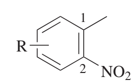


R	Time (h)		Refs.
4-F	3	(74)	516
5-F	3	(56)	516
4-Cl	3	(69)	516
5-Cl	3	(86)	516
6-Cl	3	(93)	516
4-MeO	3	(71)	516
4-NC	15.5	(68)	517

C$_{9-10}$



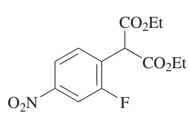
A. DMSO, H_2O, NaCl, 160–170°
B. DMA, $MgCl_2$•$6H_2O$, reflux



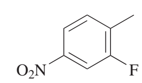
R	Cond.	Time (h)	[d]
H	A	24	(35)
H	B	24	(77)
5-F	A	48	(50)
5-F	B	20	(73)
4-Cl	A	24	(55)
4,5-Cl_2	A	12	(60)[j]
5-Me	B	12	(80)

518

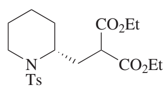
C$_9$



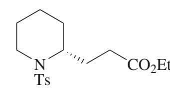
DMA, $MgCl_2$•$6H_2O$, reflux, 24 h



(65)[d] 518



DMSO, H_2O, 160°, 1 h

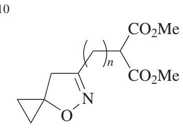


(91) 519

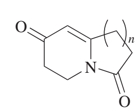
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{9-10}$



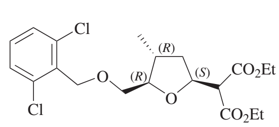
DMF, H_2O, NaCl, reflux, 6 h



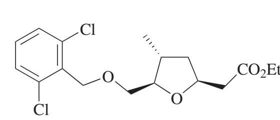
n	
1	(33)
2	(44)

520, 521

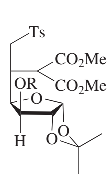
C$_9$



DMSO, H_2O, LiCl, 160°, 7 h

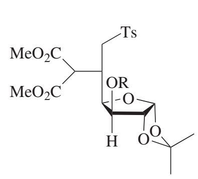


(77) 522



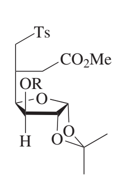
I

+



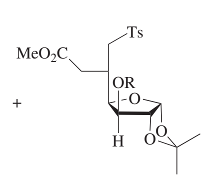
II

DMSO, H_2O, NaCl, 130°, 24 h



III

+

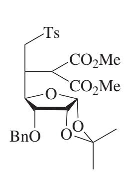


IV

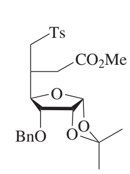
III/IV = —

R	I/II	III + IV
Me	9:1	(77)
Bn	5:1	(75)

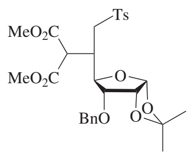
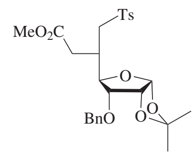
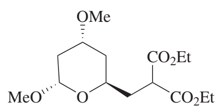
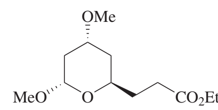
523



DMSO, H_2O, NaCl, 130°, 24 h



(74) 523

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 130°, 24 h	 (70)	523
	See table.		524

Solvent	Additive(s)	Temp (°)	
DMSO	H_2O	180	(0)[k]
dioxane	H_2O, Al_2O_3	reflux	(0)[l]

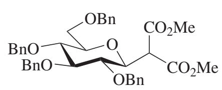
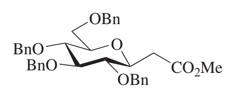
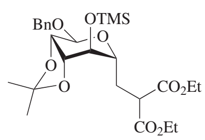
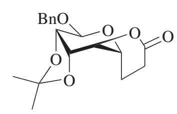
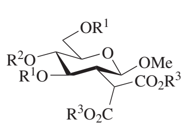
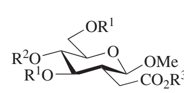
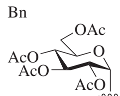
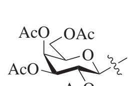
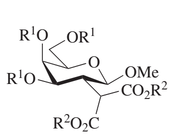
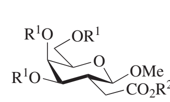
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 180°, 3 h	 (82)	525
	DMSO, H_2O, NaCl, 145°, 15 h	 (70)	239

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-15} 	DMSO, additive(s)		

R^1	R^2	R^3	Additive(s)	Cond.	Time		Refs.
Ac	Ac	Me	H_2O	180°	24 h	(0)	483
Ac	Ac	Me	LiI	180°	4.5 h	(92)	89
Ac	Ac	Me	LiI	9.9 atm, Mw (200 W), 100°	5 min	(97)	89
Ac	Ac	Me	H_2O, NaCl	180°	6 h	(34)	483
Ac	Ac	*i*-Pr	LiI	9.9 atm, Mw (200 W), 100°	5 min	(78)	89
Bn	Bn	Me	LiI	180°	5–7 h	(64)	89
Bn	Bn	Me	LiI	Mw, 100°	10–20 min	(92)	89
Ac		Me	LiI	180°	6 h	(73)	89
Ac	"	*i*-Pr	LiI	180°	6 h	(74)	89
Bn	"	Me	LiI	9.9 atm, Mw (200 W), 100°	10–20 min	(81)	89
Ac		Me	LiI	180°	6 h	(72)	89
Ac	"	*i*-Pr	LiI	180°	6 h	(71)	89
Bn	"	Me	LiI	9.9 atm, Mw (200 W), 100°	10–20 min	(79)	89

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	A. DMSO, LiI, 180°, 5–7 h B. 9.9 atm, Mw (200 W), 100°, 10–20 min		89, 483

R^1	R^2	Cond.	
Ac	Me	A	(81)
Ac	*i*-Pr	A	(80)
Bn	Me	B	(85)

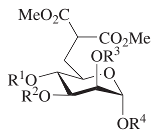
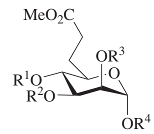
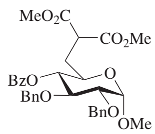
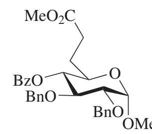
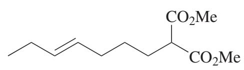
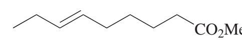
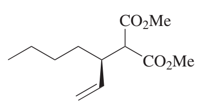
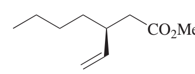
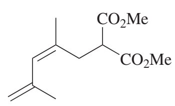
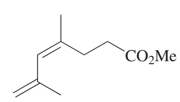
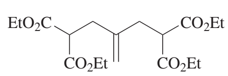
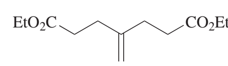
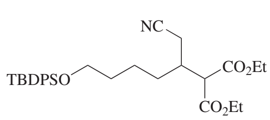
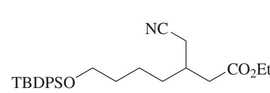
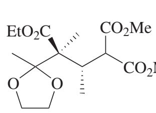
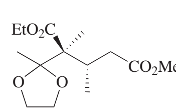
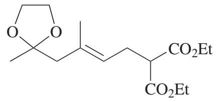
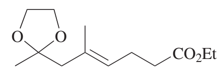
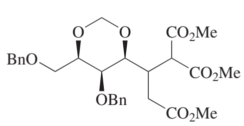
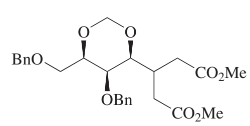
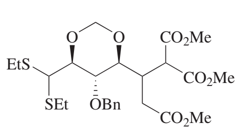
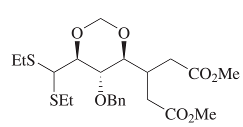
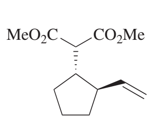
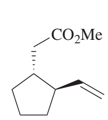
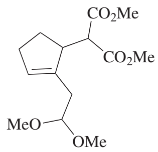
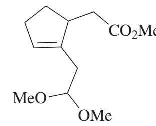
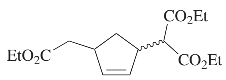
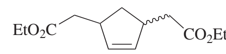
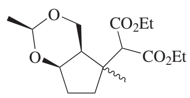
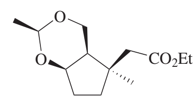
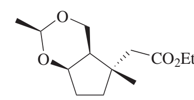
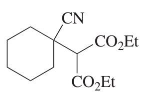
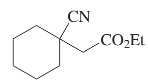
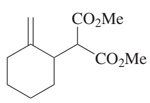
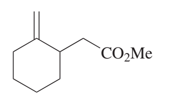
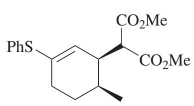
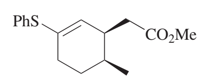
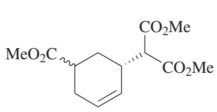
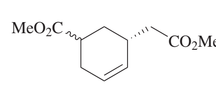
	DMSO, H_2O, NaCl, 160°, 3 h	 R^1 / R^2 / R^3 / R^4: CH_2=$CHCH_2$ / —CMe_2— / Me (80) MOM / MOM / MOM / Bn (87)[d] Bz / —CMe_2— / Bn (72)[d] Bz / Bz / Bz / Bn (14)[d]	481
	DMSO, H_2O, NaCl, 160°, 3 h	 (86)	481
C_{10}			
	DMF, H_2O, LiCl, reflux, 5 h	 (72)	526
	DMF, LiCl, KCN, 100°	 (—) >97.5:2.5 er	527
	DMSO, H_2O, NaCN, 110°, 24 h	 (60)	507
	DMSO, H_2O, LiCl	 (35)	528

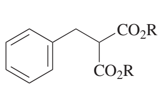
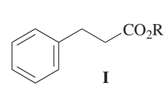
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	DMSO, LiI, 170°, 2 h	 (67)	529
	DMSO, NaCN	 (73)	530
	DMSO, H_2O, NaCl, 165°, 8 h	 (55)	531
	DMSO, H_2O, NaCl, 160°, 1 h	 (89)[d]	532, 533
	DMSO, NaCl	 (42)[d]	534
	DMSO, H_2O, NaCl, 160°, 36 h	 (40)	535

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, reflux, 5 h	 (86)	536
	DMSO, H_2O, LiCl, reflux, 6 h	 Config. *cis* (80) *trans* (43)	537
	DMSO, H_2O, LiCl, 190°, 5 h	 (14) +  (37)	538, 539
	DMSO, H_2O, LiCl, 150°, 22 h	 (74)	540
	HMPA, $Me_4N^+AcO^-$, 100°[m]	 (—)	541
	DMSO, H_2O, LiCl, 100°, 12 h	 (78)	542

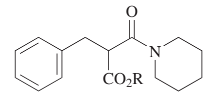
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	See table.		

Config.	Solvent	Additive	Temp (°)	Time (h)		Refs.
cis	DMSO	KOAc	115	—	(—)	118
cis	HMPA	$Me_4N^+AcO^-$	100	9	(75)	543
trans	HMPA	$Me_4N^+AcO^-$	95	20	(75)	544

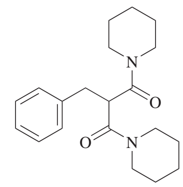
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	See table.	 **I**	

R	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
Me	DMSO	H_2O, LiCl	160	22	(84)	115
Me	[bmim]Br	LiCl	160	2	(99)	115
Et	DMSO	H_2O	reflux	4	(61)	15
Et	DMSO	H_2O, NaCl	155–170	3	(90–95)	333, 545, 546
Et	DMF	H_2O	160, Mw	0.3	(92)	17
Et	DMF	Triton B	80	3	(65)	328
Et	DMF	$4\text{-}H_2NC_6H_4SH$, Cs_2CO_3	85	3	(93)[n]	304, 547
Et	$EtCO_2H$	—	reflux	48	(85)	322
Et	$n\text{-}C_{17}H_{35}CO_2H$	$(n\text{-Bu})_4PI$	200	4	(98)	321
Et	*o*-xylene	DABCO	reflux	6	(42)	291
Et	*o*-xylene	DBN	reflux	25	(34)	291
Et	—	B_2O_3	170–190	4	(88)	311

PhMe, piperidine, reflux, 48 h

I + 

II

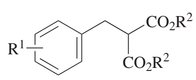
\+ 

III

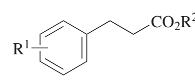
R	I	II + III
Me	(100)	(0)
Et	trace	(>98)

302

C_{10-16}

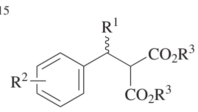


See table.

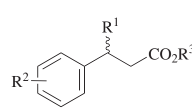


R^1	R^2	Solvent	Additives	Temp (°)	Time (h)		
H	Et	DMSO	H_2O, NaCl	180	3	(9)	546
4-Cl	Et	DMSO	H_2O, KOAc	reflux	—	(—)	548
2,6-Br_2	Et	DMSO	H_2O, NaCl	180	1	(100)	549
2-I	Et	DMSO	H_2O, NaCl	180	15	(95)	550
2-Me, 3-O_2N	Me	DMF	H_2O, LiI	160	7	(76)	551
4-CF_3	Et	DMSO	H_2O, NaCl	175	6	(—)	552
2-Cl, 4-NC	Et	DMSO	H_2O, NaCl	135–170	3	(84)	553
2,4,5-Me_3, 3,6-$(MeO)_2$	Me	DMSO	H_2O, NaCl	reflux	4	(79)	554
2-allyl, 4-MeO	Et	DMSO	H_2O, NaCl	160	10	(92)	555
3-Ph	Me	DMSO	H_2O, LiCl	165	3	(81)	556

C_{10-15}

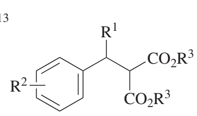


See table.

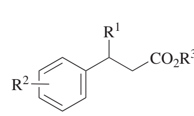


R^1	R^2	R^3	Config.	er	Solvent	Additive(s)	Temp (°)	Time		er	
MeO_2CNH	H	Me	(*R*)	96.5:3.5	DMSO	H_2O	Mw, 160	10 min	(80)	92.5:7.5	78
BocNH	H	Me	(*S*)	—	DMSO-d_6	H_2O	160	12 h	(68)	94.5:5.5	557
BnO_2CNH	H	Me	(*S*)	—	DMSO-d_6	H_2O	160	12 h	(90)	96.0:4.0	557
BzNH	H	Me	(*R*)	81.5:18.5	DMSO	H_2O	180	12 h	(91)	81.5:18.5	79
CH_2=CH	4-Cl	Me	(*R*)	—	DMSO	H_2O, NaCl	Mw, 200	20 min	(94)	—	558
CH_2=CH	2,4,6-$(MeO)_3$	Me	(*R*)	—	DMSO	H_2O, NaCl	160	—	(83)	—	559
Et	H	Et	(*R*)	—	DMSO	H_2O, LiCl	160	15 h	(100)	82.0:18.0	560
$AcCH_2$	H	Me	(*S*)	—	DMSO	H_2O, NaCl	—	—	(—)	—	562
$AcCH_2$	H	Et	(*S*)	—	DMSO	H_2O, NaCl	—	—	(—)	—	562
$AcCH_2$	H	*i*-Pr	(*S*)	—	DMSO	H_2O, NaCl	—	—	(—)	—	562
(*E*)-(*i*-Pr)CH=CH	H	Me	(*S*)	—	DMSO	NaCl	180	—	(—)	—	561

C_{10-13}



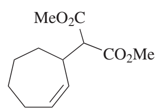
See table.



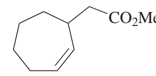
R^1	R^2	R^3	Solvent	Additives	Temp (°)	Time (h)		
$PhMe_2Si$	H	Me	DMSO	H_2O, LiCl	140	3.5	(72)	563
Me	H	Et	DMSO	H_2O, KOAc	reflux	—	(—)	548
Me	4-Cl	Et	DMSO	H_2O, KOAc	reflux	—	(73)	548
Me	4-NO_2	Et	DMSO	H_2O, KOAc	reflux	—	(—)	548
$(PMB)_2NSO_2CH_2$	2-MeO, 4-Br	Me	DMF	H_2O, NaCl	reflux	5	(—)	564

Et	H	Et	DMSO	H_2O, KOAc	reflux	—	(—)	548
Et	Cl	Et	DMSO	H_2O, KOAc	reflux	—	(—)	548
MeO_2CCH_2	4-Cl	Me	DMSO	H_2O, NaCl	reflux	overnight	(82)	565, 566, 567
MeO_2CCH_2	2,4-Cl_2	Me	DMSO	H_2O, NaCl	reflux	overnight	(80)	565
MeO_2CCH_2	3-Me, 4-BnO	Me	DMSO	H_2O, NaCl	reflux	—	(82)[d]	568
(*E*)-MeCH=CH	H	Me	DMF	LiI, NaCN	120	15	(56)	569

C_{10}

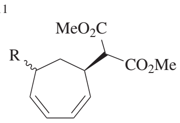


DMSO, H_2O, NaCN

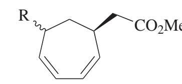


(70–90) 462

C_{10-11}

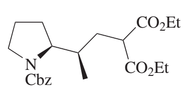


See table.

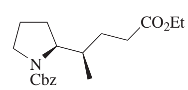


R	Config.	Solvent	Additives	Temp (°)	Time		Refs.
H	—	DMSO	H_2O, NaCN	70	36 h	(70)	306, 508
BnO	*cis*	DMF	PATP, Cs_2CO_3	85	15 min	(79)	305
BnO	*trans*	DMF	PATP, Cs_2CO_3	85	15 min	(79)	305
Me	*cis*	DMSO	H_2O, NaCN	70	36 h	(60)	306

C_{10}



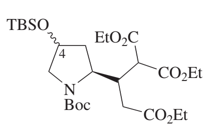
DMSO, H_2O, NaCl, 170°, 10 h



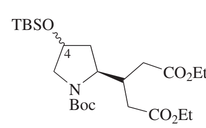
(80) 570, 571

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

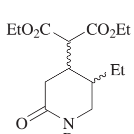
C_{10}



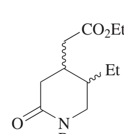
DMSO, H_2O, NaCl, 160°



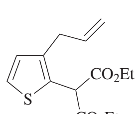
C-4 Config.	Time (h)		Refs.
(*R*)	1	(88)[d]	572
(*S*)	3	(94)[d,o]	573



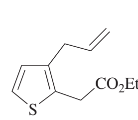
DMSO, additives



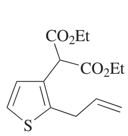
R	Config.	Additives	Temp (°)	Time (h)		Refs.
H	*cis*	H_2O, NaCl	160	3	(88)	574
H	*trans*	H_2O, NaCl	160	3	(92)	574
3-indolyl-$(CH_2)_2$	*trans*	H_2O, $MgCl_2$•$6H_2O$	reflux	—	(90)	577
3,4-$(MeO)_2C_6H_3(CH_2)_2$	*trans*/*cis* = 91:9	H_2O, NaCl	160–165	8	(85)	575, 576
3,4-$(MeO)_2C_6H_3(CH_2)_2$	*trans*	H_2O, $MgCl_2$•$6H_2O$	reflux	—	(91)	577



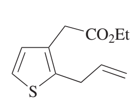
DMSO, H_2O, NaCl, 150–155°, 8 h



(80) 578



DMSO, H_2O, NaCl, 155°, 9 h



(71) 578

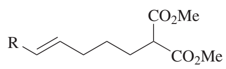
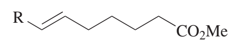
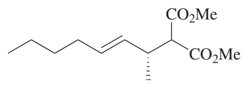
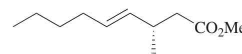
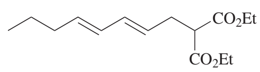
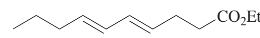
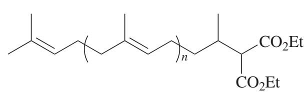
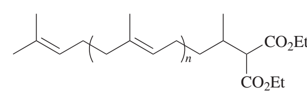
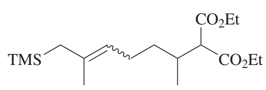
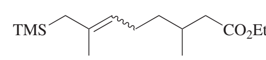
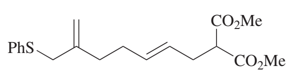
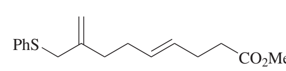
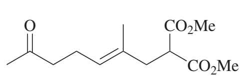
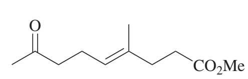
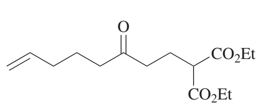
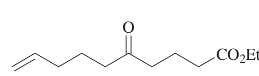
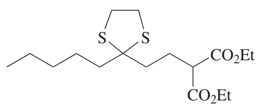
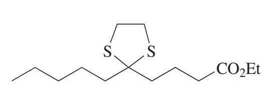
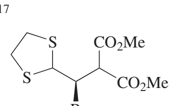
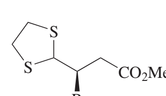
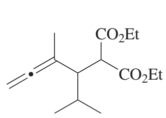
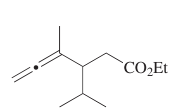
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12}			
	DMSO, H_2O, NaCl, 170°, 3 h	 R: *i*-Pr (91); *i*-Bu (93); *s*-Bu (86)	579
C_{11}			
	DMF, LiI, KCN, 110°	 (—) >97.5:2.5 er	527
	DMSO, NaCN, reflux, 4 h	 (57)	580
C_{11-21}			
	DMF, LiI, 150°, 4 h	 *n*: 0 (71); 1 (71); 2 (72)	443
C_{11}			
	DMSO, H_2O, LiCl, 185°	 (80) (*Z*)/(*E*) = 7:1	581
	HMPA, NaI	 (87)	582

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMSO, H_2O, LiCl, 130–160°, 6 h	 (65)	583
	HMPA, H_2O, NaI, 180°	 (79)	584
	DMSO, H_2O, NaCl, 155–160°, 4 h	 (83)	254
C_{11-17}			
	DMSO, H_2O, NaCl, 150°, 2–3 h	 R: 4-$O_2NC_6H_4$ (63–81); (3,4-OCH_2O)C_6H_3 (63–81); $PhCH_2CH_2$ (81); 4-PhC_6H_4 (63–81)	585
C_{11}			
	DMSO, NaCN, 160°, 4 h	 (40)	586

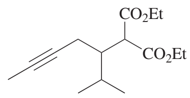
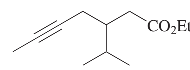
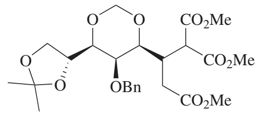
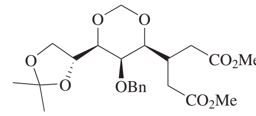
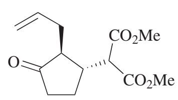
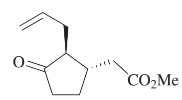
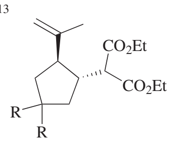
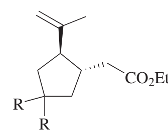
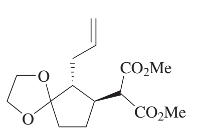
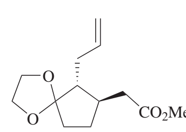
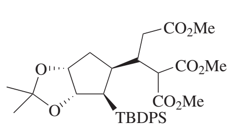
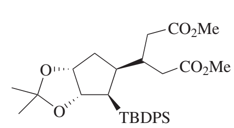
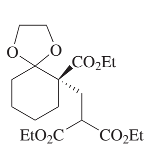
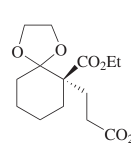
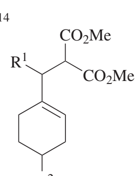
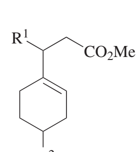
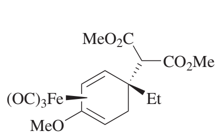
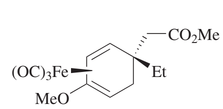
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, NaCN, 160°, 4 h	 (—)	586
	DMSO, NaCl	 (55)[d]	534
	DMSO, H_2O, 185°, 3 h	 (70)	587
C_{11-13}			
	DMSO, H_2O, LiCl, 168–170°, 6 h	 R: H (82); Me (85)	588

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMSO, H_2O, NaCl, 150°, 5 h	 (65)	589
	DMSO, H_2O, NaCl	 (—)	590
	DMSO, H_2O, NaCN, 160°, 6 h	 (80)	485
C_{11-14}			
	DMF, LiI•$3H_2O$, NaCN, 120°, 12 h	 R^1 R^2: Me H (100); H *t*-Bu (80)	541
C_{11}			
	HMPA, $Me_4N^+AcO^-$, 95°, 12 h	 (51)	262

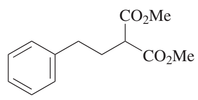
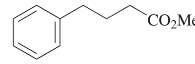
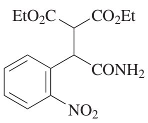
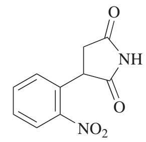
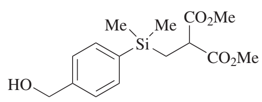
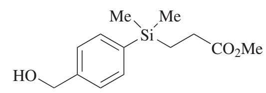
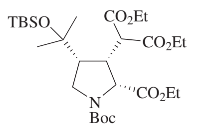
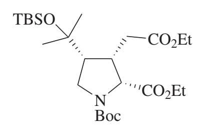
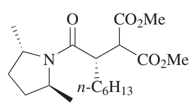
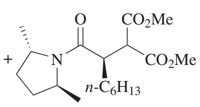
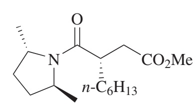
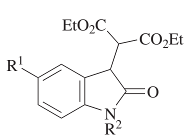
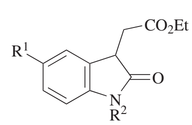
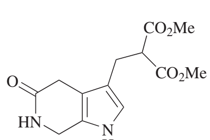
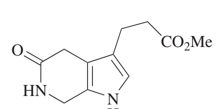
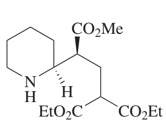
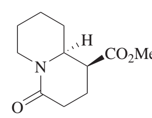
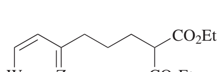
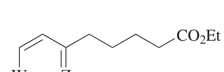
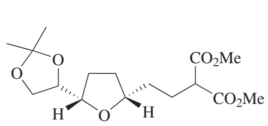
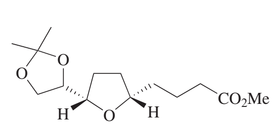
	DMF, H_2O, Mw, 180°, 30 min	 (95)	17
	DMSO, NaCl, 145–148°, 7 h	 (61)	176
	DMF, H_2O, LiCl, 140°, 24 h	 (74)	591
	DMSO, H_2O, NaCl, 170°, 2 h	 (67)	592
 + 	DMSO, H_2O, NaCl, 180°	 (—) 16:1 dr	593

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMSO, H_2O, 140°, 5 h	 R^1 / R^2: H / Me (74) H / allyl (69) H / Bn (75) MeO / Bn (76)	132
	DMSO, H_2O, NaCN, 130–140°, 24 h	 (63)	594, 595
	DMSO, H_2O, NaCl, "heat"	 (57)[d]	175
	DMSO, H_2O, NaCl	 W / Y / Z: CH / CH / N (76) CH / N / CH (93) N / CH / CH (96)	596
	DMSO, H_2O, NaCN, 115°, 2 h	 (90)	597

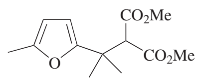
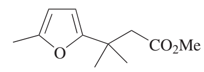
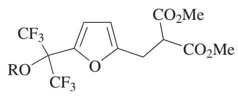
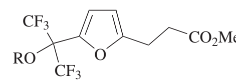
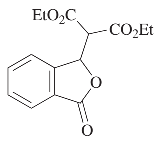
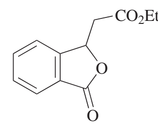
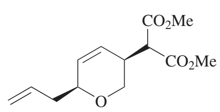
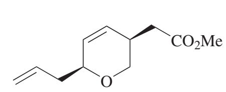
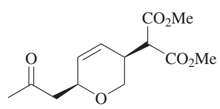
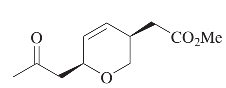
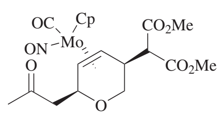
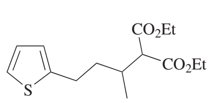
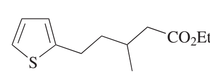
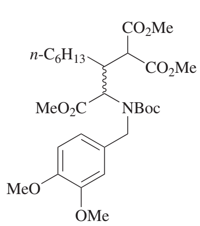
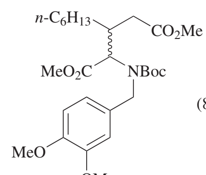
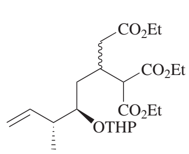
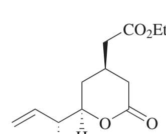
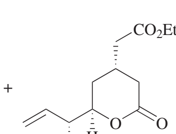
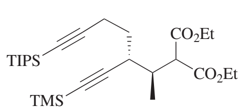
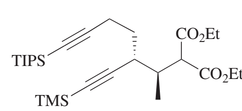
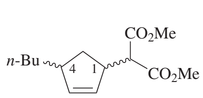
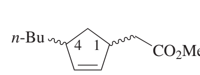
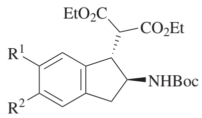
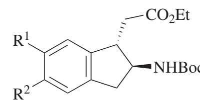
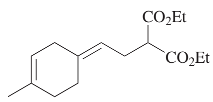
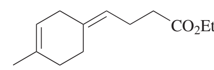
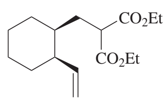
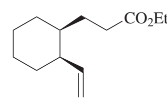
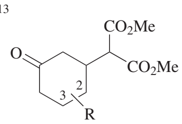
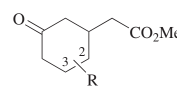
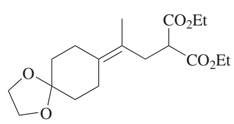
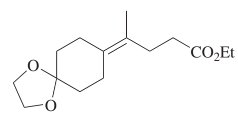
	DMF, LiI, reflux, 5 h	 (48)	598
	DMF, H_2O, LiCl, 160–165°, 4 h	 R: H (48); TMS (48)[p]	599
	DMSO, H_2O, NaCl, 130°, 5 h	 (74)	600
	DMSO, H_2O, LiCl, reflux, 1.5 h	 (56)	601
	DMF, PATP, Cs_2CO_3, 80°, 15 min	 **I** (75) 98.0:2.0 er	263
	DMSO, H_2O, NaCl, 170°, 3 h	**I** (60) 98.0:2.0 er	263

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

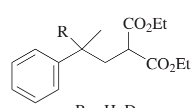
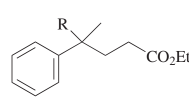
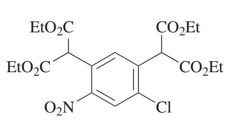
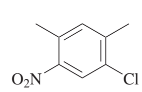
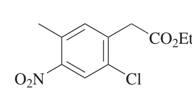
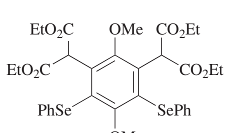
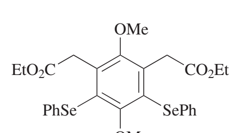
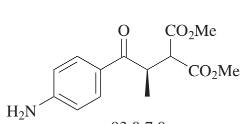
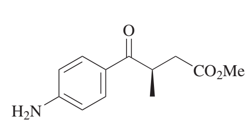
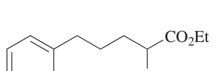
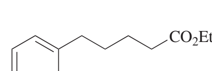
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMSO, NaCN, 160°, 7 h	 (64)	602
C_{12}			
	DMSO, NaCl, 140°, overnight	 (89)	603
	DMSO, H_2O, NaCl, 175°, 8 h	 **I** +  **II** **I** + **II** (65), **I/II** = 85:15	172
	DMSO, H_2O, LiCl, 135°, 10 h	 (—)	604
	DMSO, H_2O, LiCl, 150°, 4 h	 Config.: (1*R*,4*R*) (97); (1*S*,4*S*) (—)	605

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 160°	 (55–85)	606
	DMSO, H_2O, NaCl, 160–165°, 8 h	 (84)	545
	DMSO, LiCl, 160°	 (97)	607
$C_{12–13}$			
	DMSO, LiI•3H_2O, reflux		493
C_{12}			
	DMSO, H_2O, NaCl, 165°, 6 h	 (70)	608

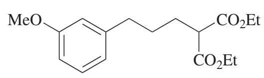
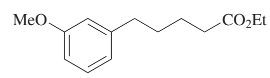
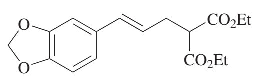
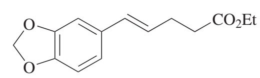
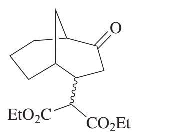
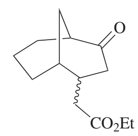
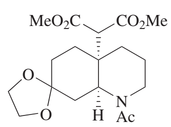
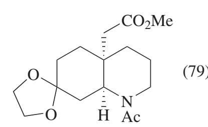
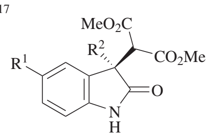
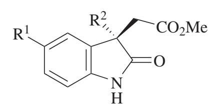
R^1	R^2
H	H
H	Br
Br	H

R	Position	
CH_2=CHCH_2	2	(64)
CH_2=CHCH_2CH_2	3	(95)

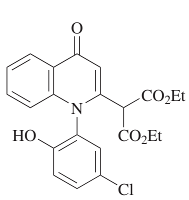
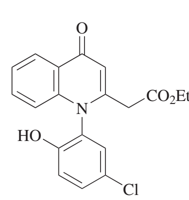
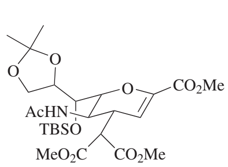
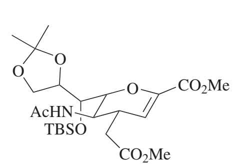
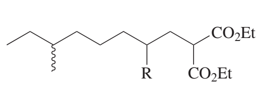
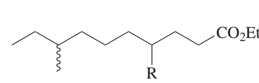
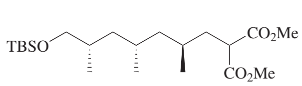
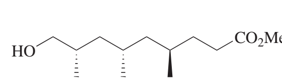
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
 R = H, D	DMSO, H_2O	 (—)	609
	DMA, $MgCl_2$•6H_2O, reflux, 7 h	 (60) +  (20)	610, 518
	HMPA, H_2O, LiCl, 100°, 3 h	 (52)	611
 >93.0:7.0 er	See table.		72
	DMF, H_2O, Mw, 180°, 0.5 h	 (96)	17

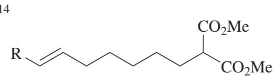
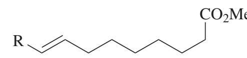
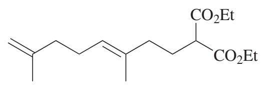
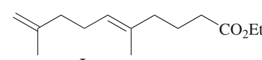
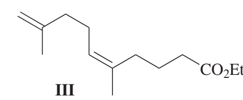
Solvent	Additives	Temp (°)	Time (h)	
DMSO	H_2O, NaCl	160	—	(—)[r]
DMF	PhOH, LiI	150	—	(—)[r]
DMSO	phosphate buffer[q], NaCl	170	2.75	(38)[s]

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, NaCN, 160°, 5 h	 (59)	612
	DMSO, H_2O, NaCl, 160–165°, 3 h	 (84)	613
	DMSO, H_2O, NaCl, 160–170°, 1 h	 (48)	614
	DMSO, H_2O, NaCN, 118°, 13 h	 (79)	615, 616
$C_{12–17}$ 	DMSO, H_2O, NaCl, 150°		136

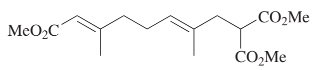
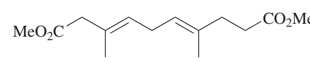
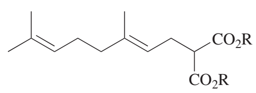
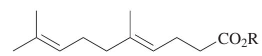
R^1	R^2	Time (h)	
MeO	$PhthNCH_2$	5	(58)
H	Ph	12	(62)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	HMPA, 120°, 2.5 h	 (94)	617
	DMSO, H_2O, NaCl, 150°, 3 h	 (62)	618
C_{13} 	DMSO, H_2O, additive, reflux		
	DMSO, H_2O, NaCl, 160°, 7 h	 (97)	621

R	Config.	Additive	Time (h)		Refs.
Me	(*S*)	KOAc	6	(98)	619
CD_3	—	LiCl	4	(53)[d]	620

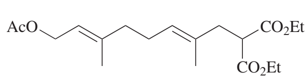
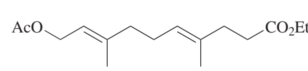
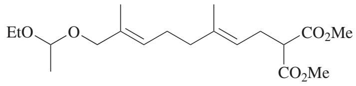
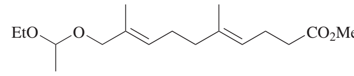
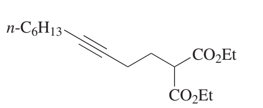
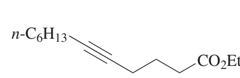
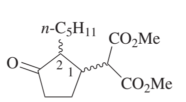
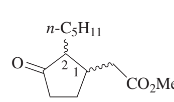
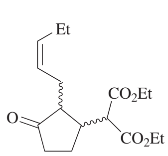
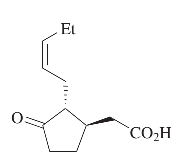
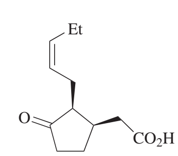
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-14} 	DMSO, H_2O, NaCl, 170°, 3 h	 R: *i*-Pr (89); *i*-Bu (89); *s*-Bu (90)	579
C_{13} 	DMSO, additive	 **I** + double bond migration isomer(s) **II** +  **III**	121, 622

Additive	Temp (°)	Time (h)	**I + II + III**	**I/II/III**
NaCN	155	16	(71)	92.8:5.4:1.8
$Me_4N^+AcO^-$	130	10	(95)	96.5:1.0:2.5

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $LiI•3H_2O$, 120°, 17 h	 (58)	623, 541, 624
	See table.		

R	Solvent	Additives	Temp (°)	Time		Refs.
Me	DMSO	H_2O, NaCl	reflux	3 h	(72)	625
Me	DMF	H_2O	Mw, 160	20 min	(84)	17
Et	DMSO	H_2O, NaCl	170	7 h	(83)	335

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	DMSO, H_2O, NaCl, 160°, 7 h	 (58)[d]	279
	HMPA, H_2O, NaI, 170°	 (—)	626
	DMSO, H_2O, LiCl, 160°, 7 h	 (76)	627
 *trans*	DMSO, H_2O, 190°, 5 h	 *trans*	628
	H_2O, 225°, 18 h [c]	 **I** +  **II**; **I + II** (50), **I/II** = 9:1	629

Config.	er		er
(1*S*,2*R*)	90.0:10.0	(63)	90.0:10.0
(1*R*,2*S*)	95.0:5.0	(60)	95.0:5.0

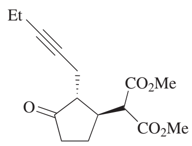
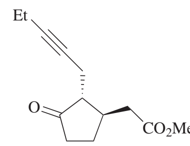
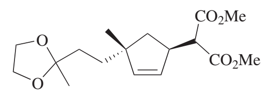
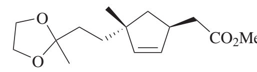
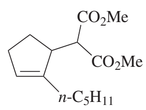
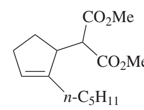
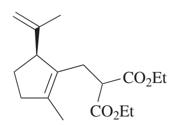
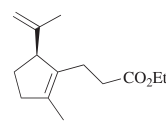
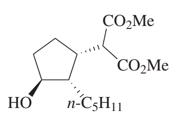
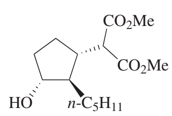
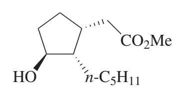
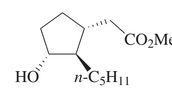
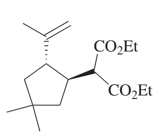
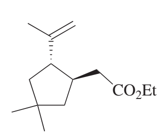
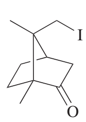
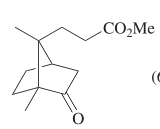
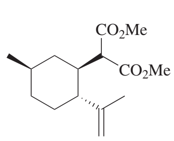
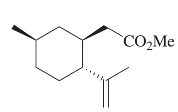
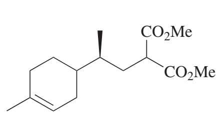
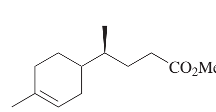
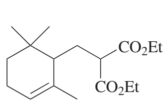
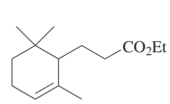
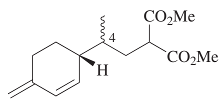
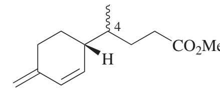
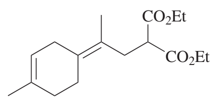
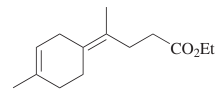
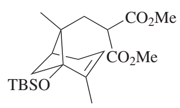
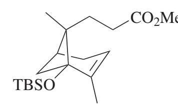
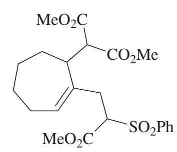
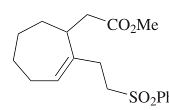
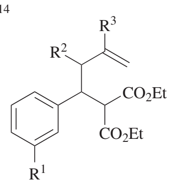
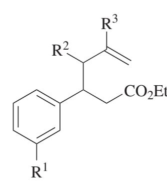
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, 165°, 2 d	 (71)	630
	DMSO, H_2O, NaCl, reflux, 1 h	 (92)	631
	DMSO, H_2O, NaCl, 160–170°, 8 h	 (77)	632
	DMSO, H_2O, NaCl, 170°, 12 h	 (76)	633
 + 	DMSO, H_2O, NaCl, 170–190°, 5 h	 +  (63)	632

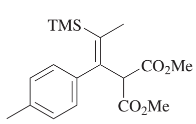
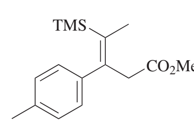
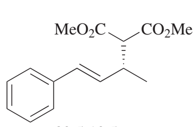
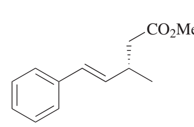
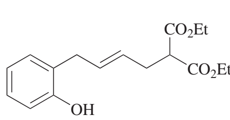
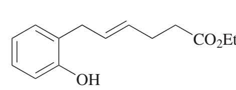
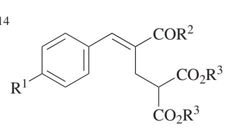
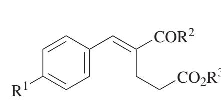
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	DMSO, H_2O, LiCl, 168–170°, 4 h	 (85)	588
 (–)-isomer	$NaCH(CO_2Me)_2$ (10 eq), DMF, reflux, 17 h	 (60)	133
	DMSO, H_2O, NaCl, 150°, 4 h	 (92)	634
	DMSO, NaCN, 130°	 (81)	635
	DMSO, H_2O, NaCl, reflux, 22 h	 (81)	636

	DMF, LiI•3H_2O, NaCN, 125°, 8 h	 Config. (4*R*) (62); (4*S*) (66)	637
	DMSO, H_2O, NaCl, 160–165°, 8 h	 (84)	638, 639
	DMSO, NaCl, H_2O, reflux, 7 h	 (80)	640
	DMF, LiI, NaCN, 130°, 24 h	 (52)	88
$C_{13–14}$			
	DMSO, H_2O, NaCl, 200°, 4–7 h		

R^1	R^2	R^3		Refs.
H	H	H	(85)	641, 642
MeO	H	H	(85)	641
H	Me	H	(85)	641
H	H	Me	(85)	641
MeO	Me	H	(80)	641
MeO	H	Me	(80)	641

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	DMF, H_2O, NaCl, Mw, 130°	 (72)	643
 89.5:10.5 er	DMF, LiI, NaCN, reflux	 (—) 89.5:10.5 er	644
	DMSO, H_2O, LiI, NaCN, 160°	 (75)	645
$C_{13–14}$			
	*p*-Xylene, additive, reflux		299

R^1	R^2	R^3	Additive	Time (d)	
H	EtO	Me	DMAP	2	(50)
H	Me	Et	DMAP	6	(45)
H	EtO	Et	DMAP	3.5	(77)
H	EtO	Et	DABCO	2	(45)
H	EtO	Et	DBN	2	"intractable mixture"
Cl	EtO	Et	DMAP	3.5	(67)
Me	EtO	Et	DMAP	3	(40)

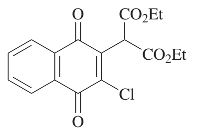
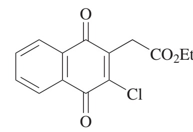
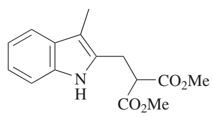
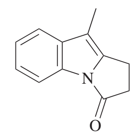
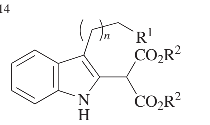
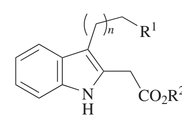
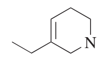
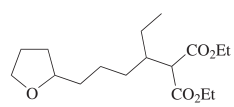
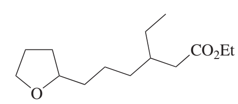
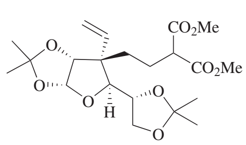
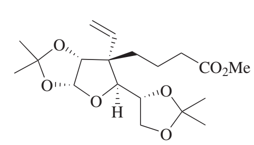
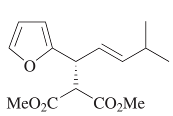
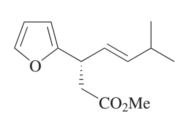
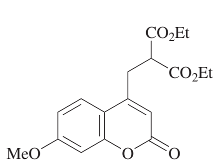
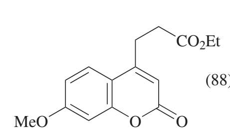
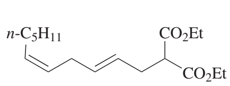
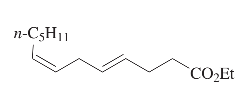
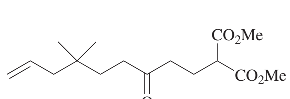
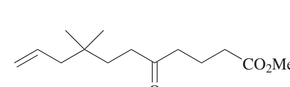
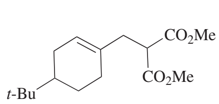
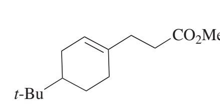
C_{13} 	DMSO, H_2O, NaCl, 110°, 3 h	 (83)	611
	DMF, H_2O, NaCl, reflux	 (—)	232
$C_{13–14}$ 	DMA, LiCl, Et_3NHCl		
		R^1 | R^2 | n | Temp (°) | Time (h) |	
		Bn_2N | Me | 1 | 130 | 2.5 | (84)	646
		 | Et | 1 | 130 | 10 | (61)	647
		Bn_2N | Me | 2 | 120–130 | 2 | (82)	648
C_{13} 	DMSO, NaCN, 160°, 4 h	 (71)	649

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	DMSO, H_2O, NaCl, 160°, 24 h	 (75)	280
	DMSO, NaCl, 180°	 (—)	561
	DMSO, H_2O, NaCl, 180°, 2.5 h	 (88)	650, 651
C_{14} 	DMSO, H_2O, NaCl, 180°, 2 h	 (58)	652
	DMSO, H_2O, NaCl, 150°, 10 h	 (87)	653
	DMF, LiI•3H_2O, NaCN, 120°, 12 h	 (100)	541

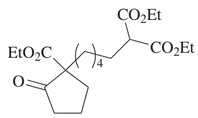
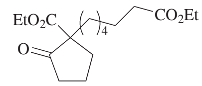
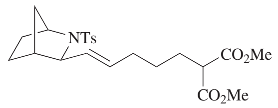
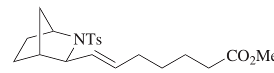
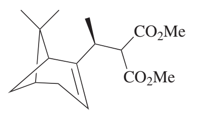
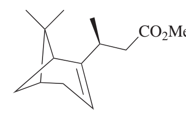
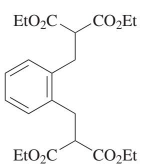
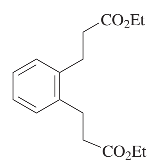
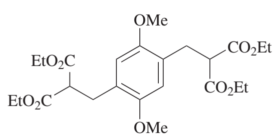
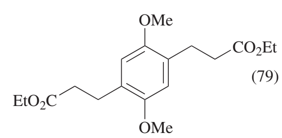
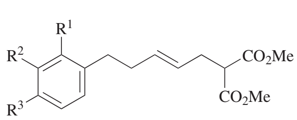
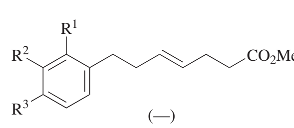
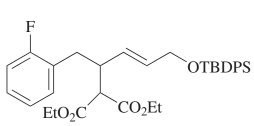
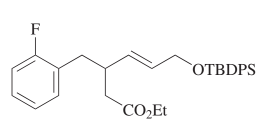
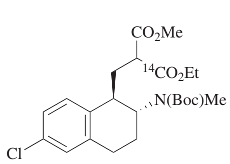
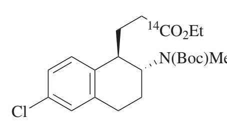
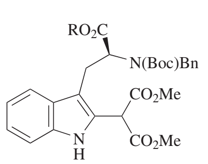
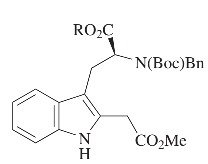
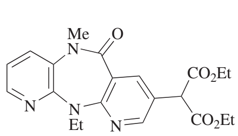
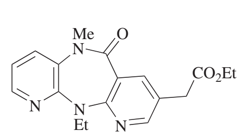
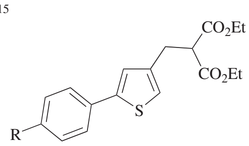
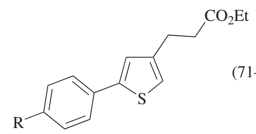
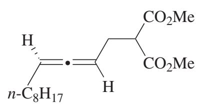
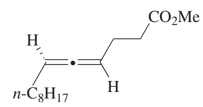
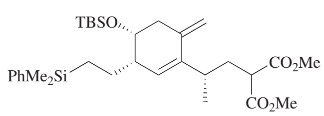
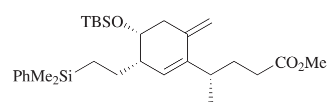
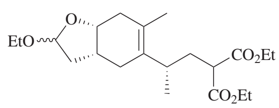
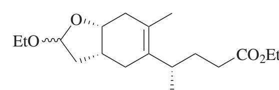
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, reflux; or DMF, LiI, heat; or collidine, *p*-cymene, heat	 (—)	86
	DMF, H_2O, LiCl, 150°, 5 h	 (75)[d]	654
	DMF, LiI, NaCN, 120°, 10 h	 (80)	541
	DMSO, H_2O, LiCl, reflux, 4 h	 (91)	655
	DMSO, H_2O, NaCl, reflux, 4 h	 (79)	656

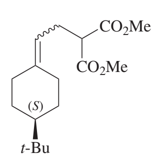
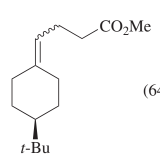
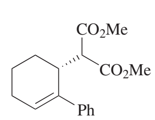
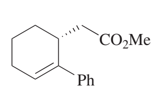
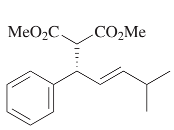
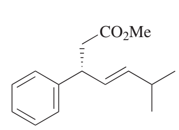
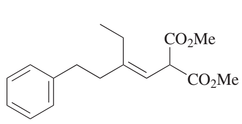
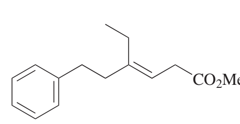
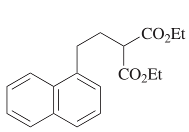
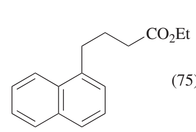
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	DMF, H_2O, NaCl, 150°	 (—) R^1 / R^2 / R^3 H / H / H H / MeO / H H / H / MeO MeO / MeO / H	657
	1. DMF, LiI, 150°, 5 h 2. H_2O, 2 h 3. LiI, 3 h	 (39)	658
	DMSO, NaCN, 85°, 8 h	 (65)	81
	DMF, H_2O, additive(s), 135°, 4 h	 R / Additive(s) Me / LiCl (82) Bn / LiCl, Et_3NHCl (85)[d]	276 659
	DMSO, H_2O, NaCl, 140°	 (63)[d]	660

C_{14-15} 	DMSO, H_2O, NaCl, reflux, 5 h	 (71–88) R: H, Cl, Br, Me	661
C_{15}  (*R*) 88.5:11.5 er	See table.		281
	DMF, PhSH, K_2CO_3, 90°, 100 min	 (89)	662, 663
	DMF, PhSH, K_2CO_3, 90°	 (38)[d]	664

Solvent	Additives	Temp (°)	Time (h)		er
DMSO	H_2O, NaCl	130	8	(35)	84.5:15.5
DMF	LiI, NaCN	120	6	(82)	77.0:23.0

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	DMF, LiI, NaCN, 120°, 16 h	 (64)	665
	DMSO, NaCl, 160°, 3 h	 (—)	666
	DMSO, H_2O, NaCl, 180°	 (—)	561
	DMSO, H_2O, NaCl, Mw, 170°	 (85)	643
	DMSO, H_2O, 200°, 5 h	 (75)	667

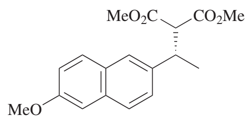
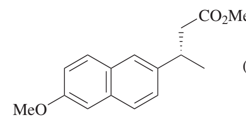
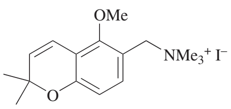
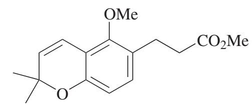
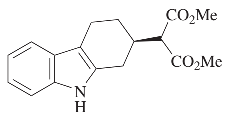
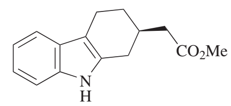
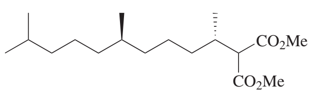
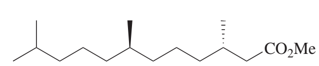
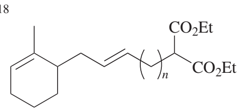
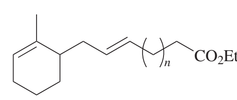
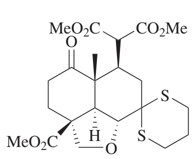
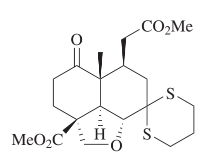
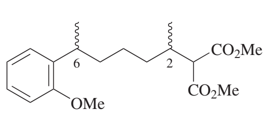
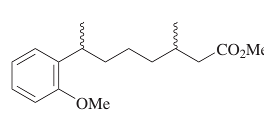
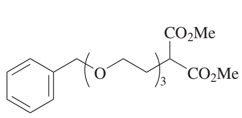
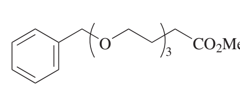
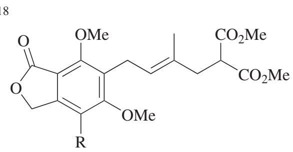
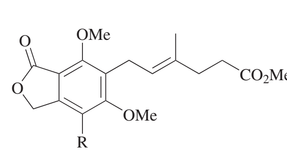
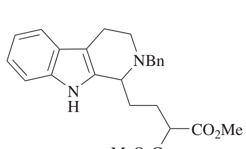
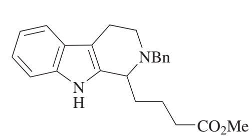
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, KOAc, 70°	 (—)	668
	DMF, $CH_2(CO_2Me)_2$, K_2CO_3, 156°, 39 h	 (75)	134
	DMSO, H_2O, LiCl, 180°, 1 h	 (92)[d] 99.5:0.5 er	138
C_{16}			
	DMSO, KOAc, 140°	 (—)	669
$C_{16–18}$			
	DMSO, H_2O, NaCl, 180°, 5 h	 *n*: 3 (90); 5 (90)	670

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	1. DMSO, H_2O, NaCl, 160°, 4 h 2. CH_2N_2	 (91)	671, 672
	DMSO, KOAc, 135°, 2.5 h	 Config.: (2*S*,6*R*) (82); (2*R*,6*S*) (—)	673
	DMSO, H_2O, NaCl, 150–160°, 4 h	 (87)	674
$C_{16–18}$			
	DMSO, H_2O, NaCl, 3 h	 R, Temp (°): H 140 (62); Me 150 (49); Et 140 (42)	675
C_{16}			
	DMSO, H_2O, LiCl, reflux, 2 h	 (73)	676

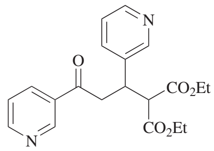
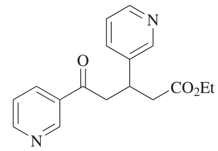
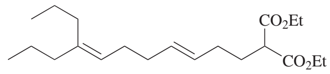
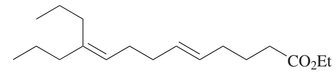
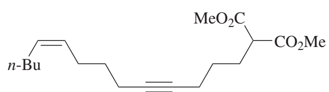
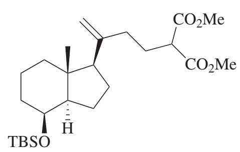
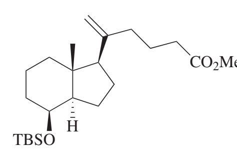
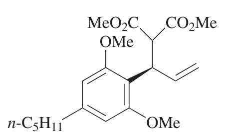
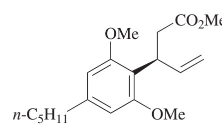
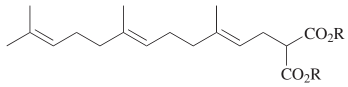
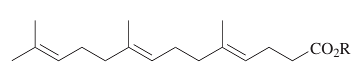
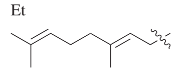
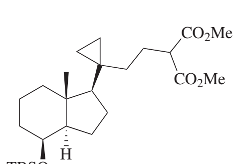
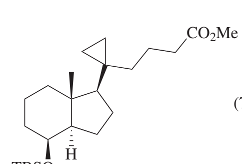
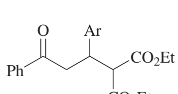
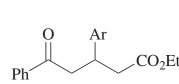
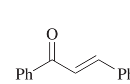
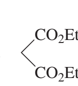
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 160°, 6 h	 (80)	677
C_{17} 	DMSO, H_2O, NaCl, 180°, 9 h	 (65)	678
	DMF, H_2O, LiCl, 160–165°, 4 h	 (70)	679
	DMSO, H_2O, LiCl, 160°, 3 h	 (87)	680
	DMSO, H_2O, NaCl, reflux	 (83)	559

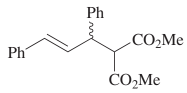
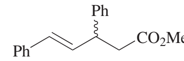
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	See table.		

R	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
Me	DMF	H_2O, NaCl	reflux	20	(91)	681, 682
Et	DMSO	NaCN	160	30	(72)	335
Et	DMSO	H_2O, LiCl	reflux	4	(56)	683, 684
Et	HMPA	H_2O, LiCl	—	—	(80)	685
	HMPA	LiCl	120	3	(85)	96

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, LiCl, 169°, 3 h	 (78)	686, 687
	See table.	 I +  II +  III	

Ar	Solvent	Additive	Temp	Time	I	II + III	Refs.
Ph	DMSO	NaCl	160°	5 h	(17)	(73)	688
Ph	DMSO	NaCl	Mw (400 W)	2 min	(16)	(84)	688
Ph	DMSO	KBr	Mw (400 W)	2 min	(0)	(94)	688
Ph	DMSO	NaI	Mw (400 W)	2 min	(0)	(97)	688
4-ClC_6H_4	DMF	—	reflux	8 h	(64)	(0)	689

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl		

Config.	Temp (°)	Time (h)		Refs.
(*R*)	170	13	(80)	391
(*S*)	180	6	(83)	690

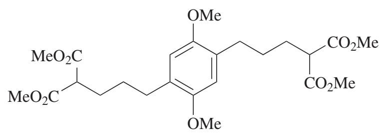
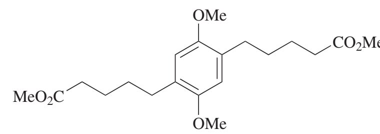
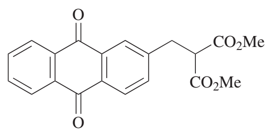
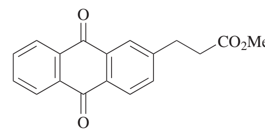
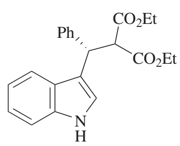
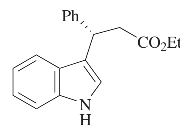
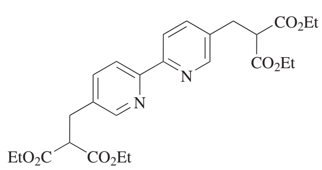
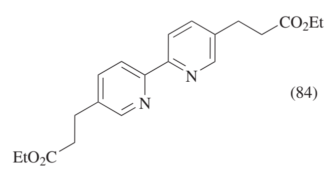
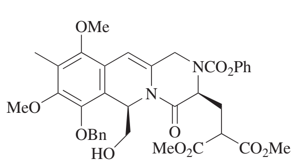
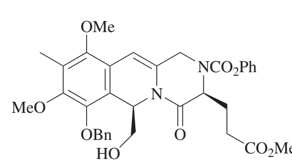
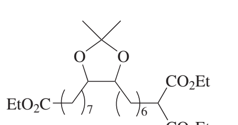
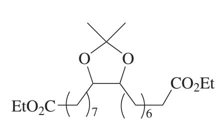
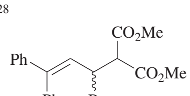
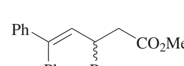
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 170°, 6 h	 (76)	691
	DMSO, H_2O, 160°, 48 h	 (60–80)	692
	DMSO, H_2O, NaCl, 160°, 18 h	 (84)	139, 693, 694, 695
	DMSO, H_2O, NaCl, reflux, 2.5 h	 (84)	696

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}			
	DMSO, H_2O, LiCl, 160°	 (67)	697
C_{19}			
	DMSO, NaCN, 160°	 (80)	698
$C_{19–28}$			
	See table.		

R	Config.	er	Solvent	Additives	Temp (°)	Time (h)		er	Refs.
Me	(*R*)	—	DMSO	H_2O, NaCl	—	—	(—)	—	699
Me	(*R*)	—	DMF	H_2O, NaCN, LiI	120	10	(100)	—	699
Me	(*S*)	97.5:2.5	DMSO	H_2O, NaCl	180	7	(81)	97.5:2.5[f]	700
2-pyridyl	(*S*)	—	DMSO	H_2O, NaCl	180	14	(72)	—	80
Ph	(*S*)	97.5:2.5	DMSO	H_2O, NaCl	180	14	(79)	97.0:3.0[f]	80, 700
$4-ClC_6H_4$	(*S*)	—	DMSO	H_2O, NaCl	180	14	(76)	—	80
$2,4,6-Me_3C_6H_2$	(*S*)	99.0:1.0	DMSO	H_2O, NaCl	180	7	(93)	—	700, 80
$1-C_{10}H_7$	(*S*)	>97.5:2.5	DMSO	H_2O, NaCl	180	7	(80)	—	700

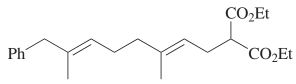
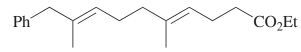
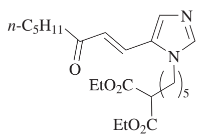
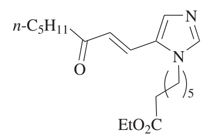
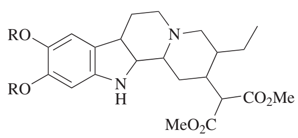
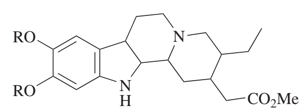
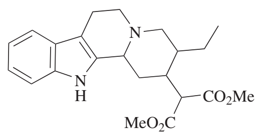
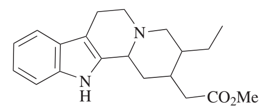
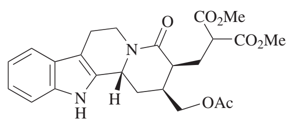
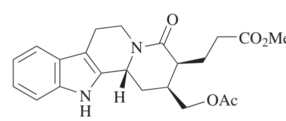
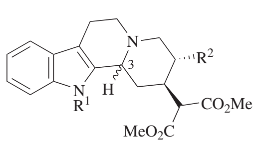
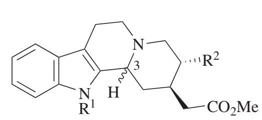
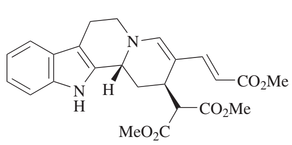
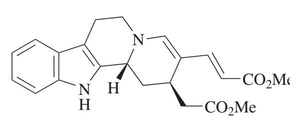
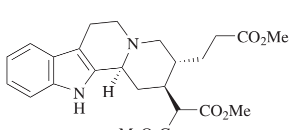
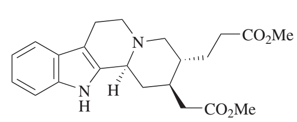
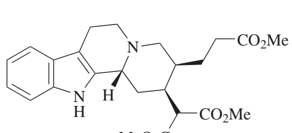
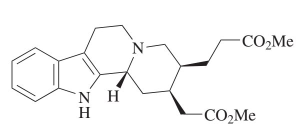
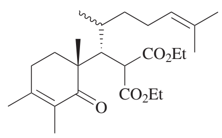
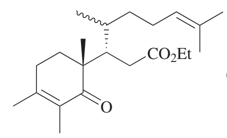
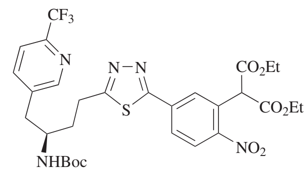
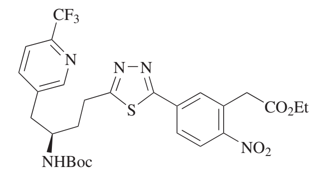
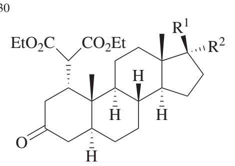
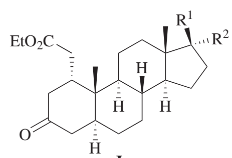
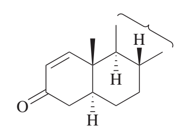
C_{19}			
	DMF, H_2O, NaCl, reflux, 24 h	 (47)	701
	DMSO, H_2O, NaCl, 160–170°, 2.5 h	 (92)	702
C_{20}			
	$EtCO_2H$, reflux, 36 h	 R H (84) Me (95)	322
	$EtCO_2H$, reflux, 24 h	 (97)	322
	DMF, LiI•$2H_2O$, reflux, 1.5 h	 (30)	703

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	DMSO, additive(s), 180°		

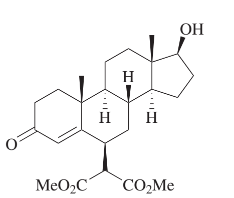
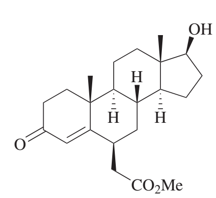
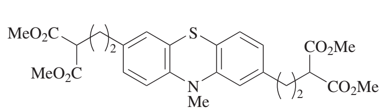
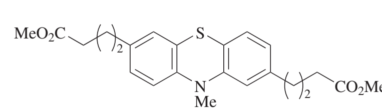
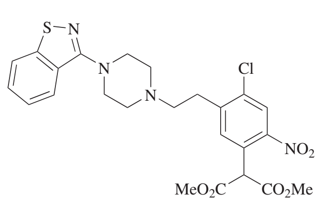
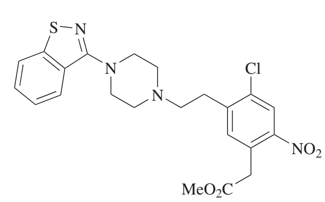
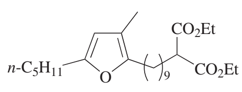
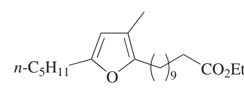
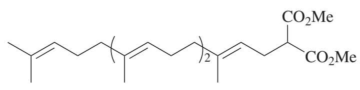
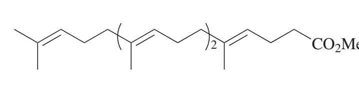
C-3 Config.	R^1	R^2	Additive(s)	Time (h)		Refs.
α	H	CH_2=CH	LiI•$3H_2O$	2.5	(65)	704
β	Bn	Et	H_2O, LiI	0.5	(70)	705

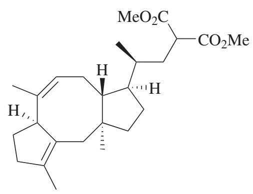
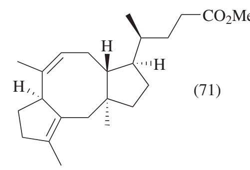
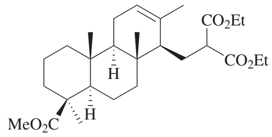
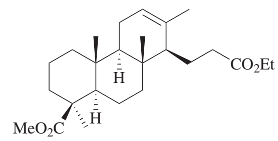
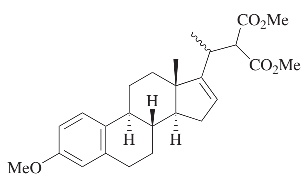
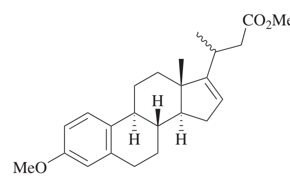
C_{21}			
	DMSO, LiI•$3H_2O$, 180°, 30 min	 (82)	708
	DMSO, LiI•$3H_2O$, 180°, 30 min	 (67)	709
	DMSO, LiI•$3H_2O$, 180°, 30 min	 (51)	709

	DMSO, H_2O, LiCl, 150°, 1 h; then reflux, 3 h	 (68)	706
	DMSO, H_2O, NaCl, 100°, 4 h	 (79)	707
C_{22-30}			
	DMSO, H_2O, NaCl, 160–180°, 4 h	 I +  II (25–35)	710, 711

R^1	R^2	I
H	AcO	(32)
HO	Me	(82)
n-C_8H_{17}	H	(69)

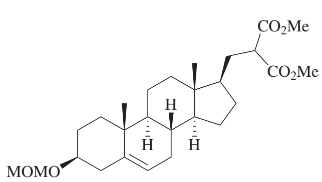
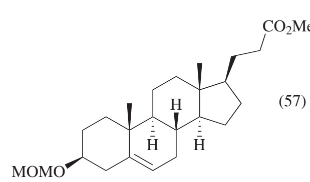
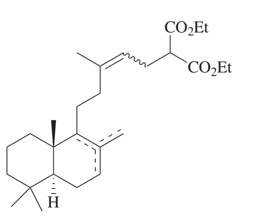
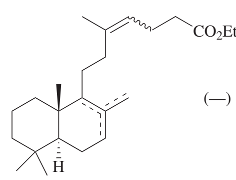
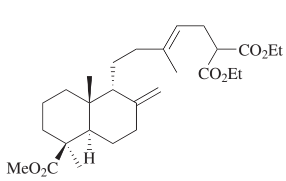
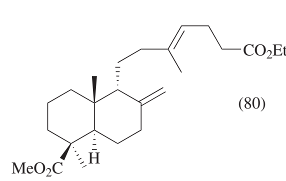
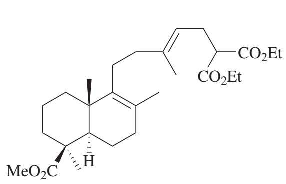
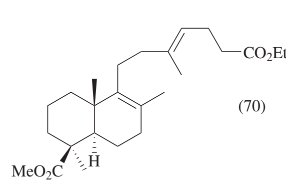
TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
	DMF, LiI, reflux, 2.5 h	 (57)	712
	DMEU, H_2O, $Me_4N^+AcO^-$, 140°, 10 h	 (80)	713
	DMSO, H_2O, LiCl	 (0)	714
	DMSO, H_2O, NaCl, reflux	 (97)	715
C_{23}			
	DMF, H_2O, NaCl, reflux, 15 h	 (82)	682

	1. DMSO, NaCN, 160°, 30 min 2. CH_2N_2	 (71)	716, 717
	DMSO, H_2O, NaCl, 180°, 4 h	 (81)	718
	See table.		719, 720

Config.	Solvent	Additive(s)	Temp (°)	Time (h)	
α	HMPA	$Me_4N^+AcO^-$	100	13	(91)
β	DMA	LiI, NaCN	—	—	(46)
β	HMPA	$Me_4N^+AcO^-$	95	13	(87)

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}			
	DMSO, NaCN, heat, 6 h	 (57)	721
	DMSO, H_2O, NaCl	 (—)	722
	DMSO, H_2O, NaCl, 180°, 14 h	 (80)	723
	DMSO, H_2O, NaCl, 180°, 14 h	 (70)	723

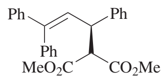
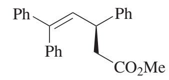
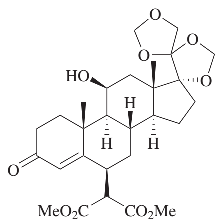
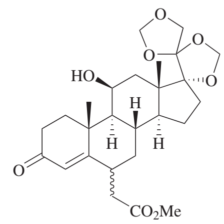
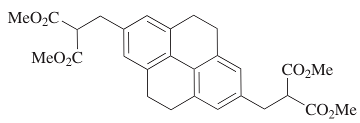
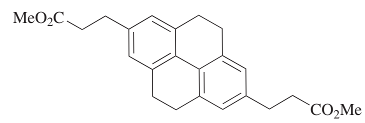
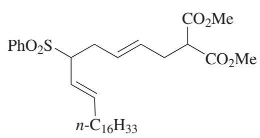
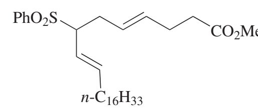
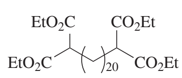
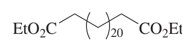
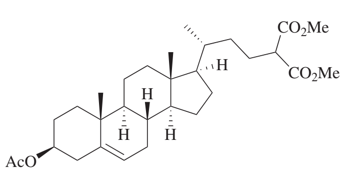
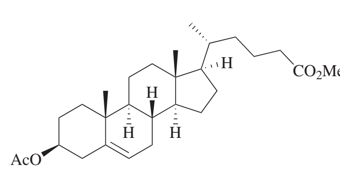
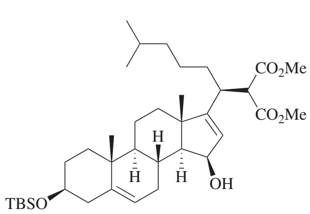
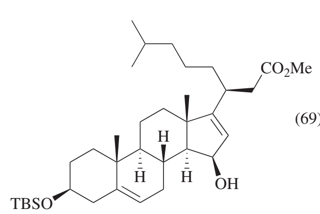
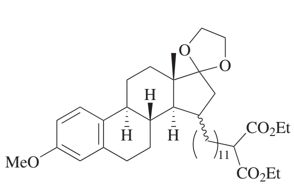
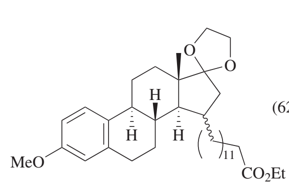
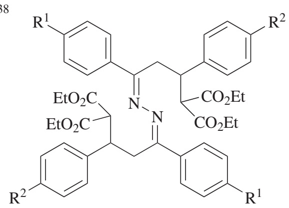
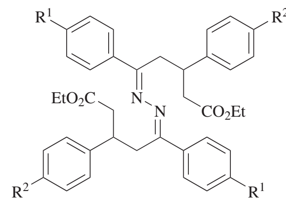
C_{24}			
	DMF, H_2O, LiI, NaCN, 120°, 10 h	 (—)	699
	DMF, LiI, 160°, 5 h	 (91)	724
	DMSO, H_2O, NaCl, 160–170°, 3 h	 (59)	725
C_{26}			
	H_2O, LiCl, 173°, 1 h	 (89)	726, 727
	DMSO, H_2O, NaCl, 140°, 24 h	 (60)	728

TABLE 2. DEALKOXYCARBONYLATIONS OF α–MONOSUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}			
	DMSO, H_2O, NaCl, 170–180°, 2.5 h	 (80)	729
C_{29}			
	HMPA, H_2O, NaI, 180°, 15 min	 (69)	140, 1276
C_{32}			
	DMF, H_2O, LiCl, reflux, 11 h	 (62)	730

Substrate		Conditions	Product(s) and Yield(s) (%)			Refs.
C_{36-38}		DMF, reflux, 6–8 h				

R^1	R^2	Yield (%)	Refs.
H	H	(55)	
H	Cl	(56)	
H	MeO	(42)	689
H	Me	(44)	
Cl	Cl	(54)	
Cl	MeO	(47)	
Cl	Me	(55)	

[a] The following additives gave yields of 96–99% under the same conditions: Li•H_2O; NaBr; NaI; NaCN; Na_2CO_3•H_2O; Na_2PO_4•12 H_2O; KCl; $CaCl_2$•2 H_2O.

[b] The following additives gave yields of 99% under the same conditions: NaCl; NaCN; Na_2PO_4•12 H_2O; KCl; $CaCl_2$•2 H_2O.

[c] The substrate has carbon-14 in the 2-position.

[d] The yield includes that of the preparation of the substrate.

[e] A small amount of the acid was also formed.

[f] The substrate has carbon-13 in the 2-position.

[g] The product is the acid after hydrolysis; the yield is for the three steps of ketal formation, dealkoxycarbonylation, and hydrolysis.

[h] The substrate contained 17% of double bond isomers.

[i] The substrate was a mixture of *o*-, *m*-, and *p*-isomers.

[j] The substrate was a mixture with diethyl 2,5-dichloro-4-nitrophenylmalonate; the latter gave 2,5-dichloro-4-nitrotoluene in 20% yield.

[k] A mixture of unidentified products was obtained.

[l] Starting material was recovered.

[m] Treatment of the starting material with NaCN in DMF at 120º gave poorer results.

[n] The product was a 2:1 mixture of ester and acid.

[o] The yield is that of the crude product.

[p] Some desilylated alcohol was also formed.

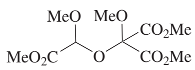
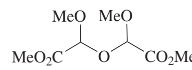
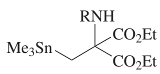
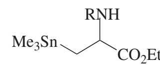
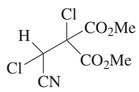
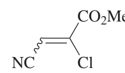
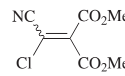
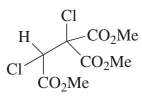
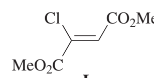
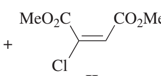
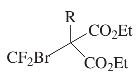
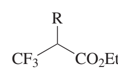
[q] The phosphate buffer was a 1.0:1.6:1.1:2.0 mixture of NaH_2PO_4/Na_2HPO_4/NaCl/H_2O.

[r] There was significant loss of enantiomeric purity in the product.

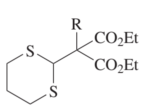
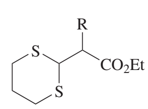
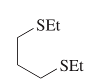
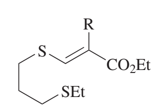
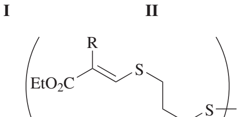
[s] There was no significant loss of enantiomeric purity in the product.

[t] The enantiomeric ratio was determined in a subsequent product.

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES

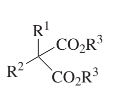
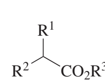
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
	DMSO, H_2O, NaCl, 130°, 2.5 h; then 160°, 1 h	 (66)	731
C_4			
	DMF, H_2O, LiCl, reflux, 12 h	 R: CHO (4); Ac (6)	732
C_5			
	Et_4NCl, vacuum distillation	 **I** +  **II**; **I** + **II** (72), **I**/**II** = 64:36	733
	Et_4NCl, vacuum distillation	 **I** +  **II**; **I** + **II** (58), **I**/**II** = —	733
C_{5-11}			
	DMSO, KF, 150°, 0.5 h; then 170°, 1–1.5 h		734

R	
Me	(44)
Et	(44)
n-Pr	(40)
n-Bu	(34)
CH_2=$CHCH_2$	(44)
$NC(CH_2)_2$	(35)
EtO_2CCH_2	(37)
Ph	(42)
Bn	(61)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-10}			
	DMSO, H_2O, NaCl, reflux	 **I** +  **II** +  **III** +  **IV**	243

R	Time (h)	**I**	**II**	**III**	**IV**
Me	4	(10)	(10)	(38)	(38)
Ph	2	(17)	(9)	(34)	(17)

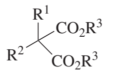
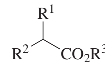
C_{5-25}

 See table. 

R^1	R^2	R^3	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
Me	Me	Me	$(MeO)_2CO$, MeOH	Et_2NMe	200	—	(86)	735
Me	Me	Et	DMSO	H_2O	reflux	21	(3)	15
Me	Me	Et	DMSO	H_2O, LiCl	reflux	4	(99)	15
Me	Me	Et	DMSO	KCN	reflux	0.5	(98)	15
CD_3	Me	Et	DMSO	H_2O, NaCl	155	—	(78)	336
CD_3	Et	Et	DMSO	H_2O, LiCl	"heat"	—	(51)	620
Et	Et	Me	DMSO	H_2O	reflux	2	(1)	15
Et	Et	Me	DMSO	H_2O, LiCl	reflux	6	(98)	15
Et	Et	Me	DMSO	H_2O, NaCl	reflux	22	(85)	15
Et	Et	Me	DMSO	H_2O, KCN	reflux	5	(95)	15

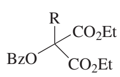
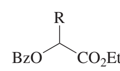
Continued on next page.

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

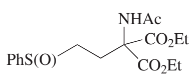
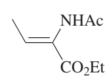
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-25} 	See table.		

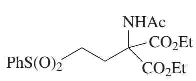
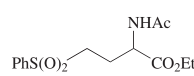
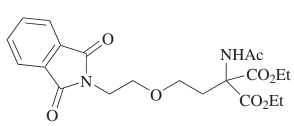
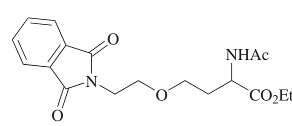
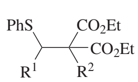
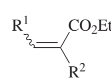
Continued from previous page.

R^1	R^2	R^3	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
Et	Et	Me	*o*-xylene	DABCO	reflux	48	(87)[a]	291
Et	Et	Me	1-oxo-1-methylphospholine	H_2O, NaCl	175	12	(89)	113
Et	Et	Me	*n*-$C_{17}H_{35}CO_2H$	(*n*-Bu)$_4$PBr	200	16	(92)	321
CD_3CH_2	CD_3CH_2	Et	DMSO	H_2O, LiCl	reflux	12	(90–95)	736
$MeCD_2$	$MeCD_2$	Et	DMSO	H_2O, LiCl	reflux	12	(90–95)	736
Et	*i*-Pr(CH_2)$_2$	Et	*o*-xylene	DABCO	reflux	48	(62)	291
n-Bu	EtO_2C	Et	DMSO	H_2O, LiCl	reflux	2	(—)	737
i-Pr	*i*-Pr	Et	1-oxo-1-methylphospholine	H_2O, NaCl	160–170	14	(68)	113
$EtCHMeCH_2$	Me	Et	DMSO	NaCN	160	7	(57)	738
Ph	Et	Et	*o*-xylene	DABCO	reflux	10	(31)	291
Bn	Bn	Et	*n*-$C_7H_{15}CO_2H$	(*n*-Bu)$_4$PBr	200	16	(75)	321
n-C_8H_{17}	Me	Et	DMSO	H_2O, LiCl	reflux	6	(86)	739
(*n*-C_6H_{13})(*n*-C_8H_{17})$CHCH_2$	*n*-C_6H_{13}	Et	DMSO	H_2O, NaCl	reflux	4	(73)	740

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-9} 	DMSO, H_2O, NaCl, 200°, 3.5 h	 **I** + $PhCO_2Et$ **II**	331

R	**I**	**II**
Et	(50)	(30)
Ph	(31)	(44)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	DMSO, LiCl, 120°, 2 h	 (38)	255

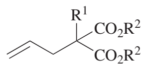
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, LiCl, 120°, 2 h	 (88)	255
	DMSO, H_2O, NaCl, 170°, 8 h	 (77)	741, 742
C_{6-16} 	See table.		248

R^1	R^2	Solvent	Additive	Temp (°)	Time (h)	[b]	(*E*)/(*Z*)
H	Et	HMPA	NaBr	135–140	5	(73)	—
Me	Et	HMPA	NaBr	135–140	5	(73)	76:24
Me	Et	HMPA	LiCl	135–140	5	(77)	75:25
Me	Et	DMF	LiCl	145–150	10	(77)	86:14
Me	Et	DMSO	LiCl	165–170	13	(77)	88:12
Me	Ph	HMPA	NaBr	135–140	5	(78)	73:27
n-Pr	Me	HMPA	NaBr	135–140	5	(86)	88:12
n-Pr	Et	HMPA	NaBr	135–140	5	(74)	84:16
n-Pr	*i*-Pr	HMPA	NaBr	135–140	5	(45)	57:43
n-Pr	*n*-Bu	HMPA	NaBr	135–140	5	(72)	79:21
n-Pr	*n*-Bu	DMF	LiCl	145–150	10	(70)	90:10
n-Pr	Ph	HMPA	NaBr	135–140	5	(59)	68:32
n-Pr	Ph	DMF	LiCl	145–150	10	(60)	81:19
Ph	Et	HMPA	NaBr	135–140	5	(68)	96:4
Ph	*i*-Pr	HMPA	NaBr	135–140	5	(64)	77:23
Ph	*n*-Bu	HMPA	NaBr	135–140	5	(54)	96:4
Ph	Ph	HMPA	NaBr	135–140	5	(66)	74:26

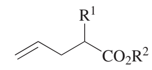
TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{6-16}

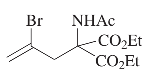


See table.

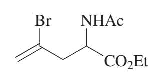


R^1	R^2	Solvent(s)	Additive(s)	Temp (º)	Time (h)		Refs.
F	Et	DMSO	H_2O, NaCl	reflux	4	(78)	743
$BnMeN(CH_2)_2$	Et	DMSO, DMF	LiCl	190	6	(97)	746
Me	Et	DMSO	H_2O, LiCl	reflux	6	(85)	744
Me	Et	DMSO	H_2O, NaCl	170–180	6	(40–80)	367, 745
Me	Me	DMSO	H_2O, LiCl	180	24	(72)	747
Et	Et	DMSO	H_2O, NaCl	170–180	6	(40–80)	367
$MeO(CH_2)_2$	Et	DMSO, DMF	LiCl	170	6	(87)	748, 749
$BnO(CH_2)_2$	Et	DMSO, DMF	H_2O, LiCl	170	6	(87)	748, 750
i-Pr	Et	DMSO	H_2O, NaCl	—	—	(25)	120
i-Pr	Et	DMSO	H_2O, KOAc	reflux	8	(99)	120
n-Bu	Me	DMSO	H_2O, NaCl	180	—	(76)	751
c-C_5H_9	Et	DMSO	H_2O, LiCl	185	6	(84)	752
Bn	Et	DMSO	H_2O, NaCl	170–180	6	(40–80)	367
2-$IC_6H_4CH_2$	Et	DMSO	H_2O, LiCl	170	8	(83)	753
(*E*)-PhCH=$CHCH_2$	Et	DMSO	H_2O, NaCl	reflux	90	(54)	754
4-*t*-BuC_6H_4	Et	DMSO	H_2O, LiCl	—	—	(48)	755

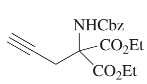
C_6



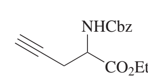
Additives, reflux



Solvent	Additives	Time (h)		Refs.
dioxane	H_2O, HCl, NaCl	24	(95)	756
DMF	H_2O, LiBr	6	(86)	757, 758, 759

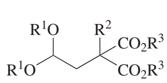


DMF, H_2O, LiBr, 155°, 12 h

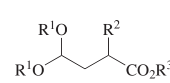


(85) 760

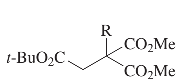
C_{6-12}



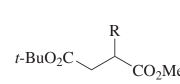
See table.



R^1	R^2	R^3	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
Me	Me	Me	DMF	LiCl	reflux	2	(69)	341
Et	Me	Et	Krapcho	—	—	—	(77)	761
Me	allyl	Me	DMF	LiCl	reflux	2	(90)	341
Et	*i*-Pr	Et	DMSO	H_2O, KOAc	130–140; then 160–170	18; 18	(78)	762
Me	Bn	Me	DMF	LiCl	reflux	2	(92)	341

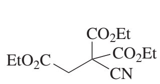


DMF, LiBr, H_2O, 135°, 8 h

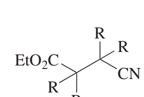


R		Refs.
Me	(33)	763
$Me_2NC(O)CH_2$	(28)	
$MeS(CH_2)_2$	(30)	
CH_2=C(Br)CH_2	(45)	
Bn	(46)	

C_6



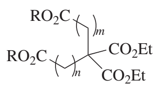
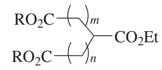
See table.



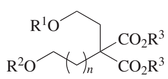
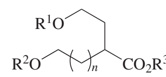
69

Solvent	Additives	Temp (º)	Time (h)	R	
DMSO	H_2O, NaCl	140	18	H	(87)
DMSO-d_6	D_2O, NaCl	180	14	D	(62)

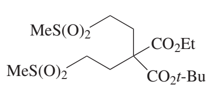
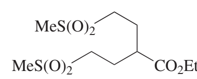
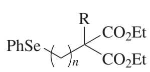
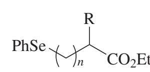
TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-9} 	DMSO, additive(s)		764

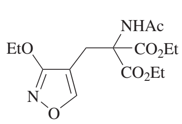
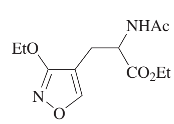
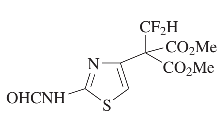
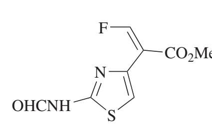
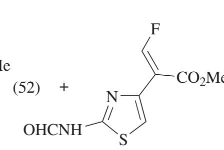
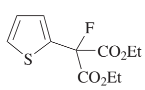
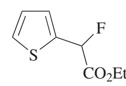
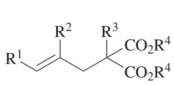
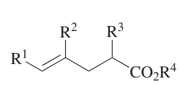
R	*m*	*n*	Additive(s)	Temp (°)	Time (h)	
Me	1	1	KCl	170–175	3.5	(90)
Et	1	2	H_2O, NaCl	185–190	5.5	(81)
Me	2	2	H_2O, NaCl	185–190	5.5	(77)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	DMSO, H_2O, additive		

n	R^1	R^2	R^3	Additive	Temp (°)	Time (h)		Refs.
1	Me	Me	Me	LiCl	185	3.5	(64)	765
1	Bn	THP	Et	NaCl	reflux	16	(28)	766
2	Me	Bn	Me	LiCl	reflux	22	(67–86)	750

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Krapcho	 (0)	90
C_{7-16} 	DMSO, H_2O, LiCl, 170°, 24 h		

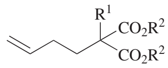
n	R		Refs.
3	Me	(80)	767
3	allyl	(93)	768
3	(*E*)-PhCH=CHCH$_2$	(96)	768
4	allyl	(88)	768
4	(*E*)-PhCH=CHCH$_2$	(93)	768

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	DMSO, H_2O, NaCl, 160°, 7 h	 (78)	769
	DMF, LiI, 160°	 (52) +  (14)	230
	DMF, LiI, 130°	 (44)	228
C_{8-13} 	See table.		

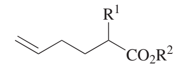
R^1	R^2	R^3	R^4	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
Me	H	Me	Et	DMSO	H_2O, NaCl	reflux	18	(20)	772
H	Br	*t*-BuO$_2$CCH$_2$	Me	DMF	H_2O, LiBr	135	6	(62)	770
H	Me	Et	Et	DMSO	NaCN	160	4	(69)	771
Cl	H	*i*-Pr	Me	DMSO	H_2O, NaCl	180	7	(75)	773
Cl	H	*i*-Pr	Me	sulfolane	H_2O, NaCl	225	13	(—)	773
TMS	H	Bn	Me	HMPA	LiCl	120	24	(60)	774

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{8-10}

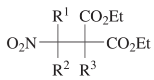


DMSO, H_2O, additive

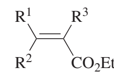


R^1	R^2	Additive	Temp (º)	Time (h)		Refs.
Me	Et	LiCl	reflux	14	(58)	416
n-Pr	Me	NaCl	180	—	(72)	751, 775
TBDPSO(CH_2)$_3$	Me	NaCl	180	5	(58)	776, 777

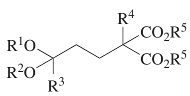
C_{8-13}



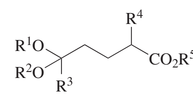
HMPA, NaBr, 130–140°



R^1	R^2	R^3	Time (h)		Refs.
Me	Me	Et	3	(80)	233
Me	Me	Et	4	(63)[c]	
Me	Me	*n*-Bu	4	(69)[c]	
Me	Me	Bn	4	(55)[c]	
—(CH_2)$_5$—		Et	3	(56)[c]	
—(CH_2)$_5$—		*n*-Bu	4	(42)[c]	

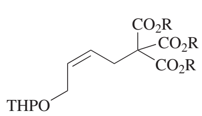


See table.

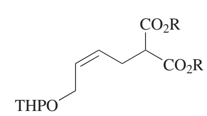


R^1	R^2	R^3	R^4	R^5	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
Me	Me	H	Et	Me	DMF	H_2O, NaCl	reflux	128	(81)	778
—(CH_2)$_2$—		H	Et	Et	DMSO	H_2O, LiCl	reflux	3	(83)	346, 779
—(CH_2)$_2$—		H	Et	Et	DMSO	H_2O, NaCl	175–180	8	(55)	780
—(CH_2)$_2$—		H	*i*-Pr	Et	DMSO	H_2O, NaCl	160	8	(66)	781
—(CH_2)$_2$—		Et	Me	Me	DMSO	KOAc	160	—	(—)	784
—(CH_2)$_2$—		Me	*i*-Pr	Et	DMSO	H_2O, NaCl	160	8	(74)	783, 782
—(CH_2)$_2$—		H	Bn	Et	DMSO	NaCl	180	—	"good"	349

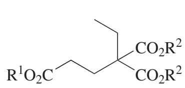
C_8



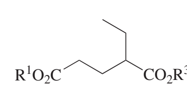
DMF, additive



R	Additive	Temp (º)	Time (h)		Refs.
Me	NaCN	90	0.5	(63)	145
Et	KCN	110	1	(76)	



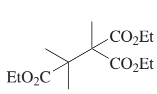
Krapcho



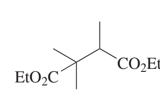
(—)

R^1	R^2
Me	Et
Et	Me
Et	Et

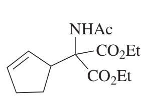
785



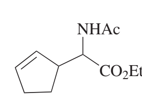
o-Xylene, DABCO, reflux, 29 h



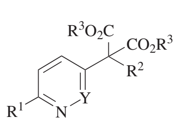
(50) 291



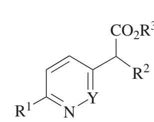
DMSO, H_2O, NaCl, 160°, 11 h [d]



(85) 786



See table.



R^1	R^2	R^3	Y	Solvent	Additives	Temp (º)	Time (h)		Refs.
Cl	Me	Et	N	DMSO	H_2O, NaCl	Mw, 175	1.5	(35)	787
Br	MeO	Me	CH	DMF	H_2O, LiBr	160	0.5	(56)	788

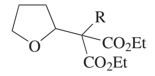
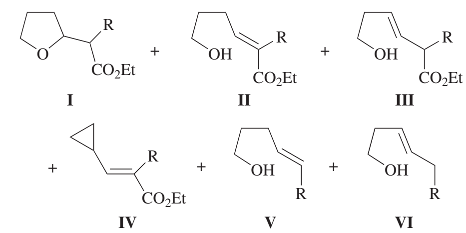
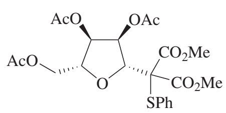
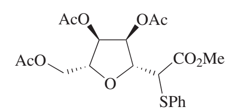
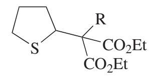
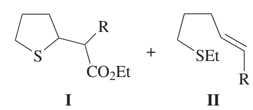
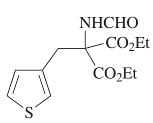
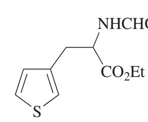
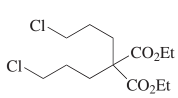
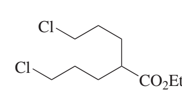
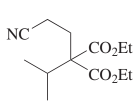
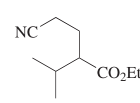
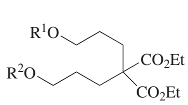
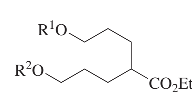
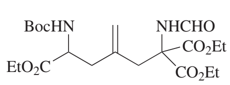
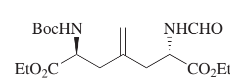
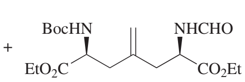
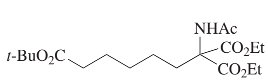
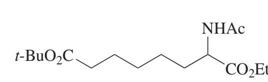
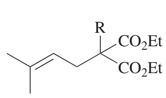
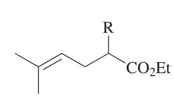
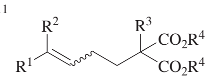
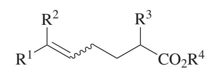
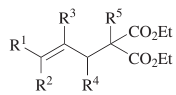
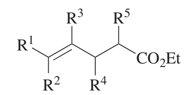
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-13} 	DMSO, H_2O, NaCl, reflux	 I + II + III + IV + V + VI R / Time (h) / I / II / III / IV / V + VI Me / 30 / (30) / (38) / (5) / (0) / (0) Ph / 10 / (37) / (0) / (18) / (4) / (15)	243
C_8 	PhH, DABCO, Me_2S, celite, reflux, 24 h	 (40) 1:1 dr	789
C_{8-13} 	DMSO, H_2O, NaCl, reflux	 I + II R / Time (h) / I / II Me / 8 / (80) / (0) Ph / 5 / (80) / (9)	243
C_8 	DMSO, H_2O, NaCl, 170–180°, 2.5 h	 (74)	790, 791
C_9 	DMSO, H_2O, NaCl	 (0)	792
	DMSO, H_2O, LiCl, reflux, 8 h	 (65)	793
	DMSO, H_2O, LiCl, 140°, 3 d	 R^1 / R^2 TBS / TBS / (55) PMB / PMB / (38) DMB / Tr / (13)	794
	DMSO, H_2O, NaCl, 160°, 2 h	 (15.5) +  (12)	795
	DMSO, H_2O, LiCl, 150°, 16 h	 (98)	141
C_{9-15} 	DMSO, H_2O, NaCl, 170–180°, 6 h	 R Me (40–80) Et (40–80) *i*-Pr (40) $Me_2C{=}CHCH_2$ (40–80) Bn (40–80)	367

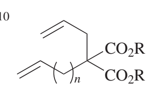
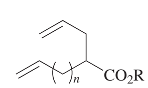
TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-11} 	DMSO, H_2O, additive, reflux		

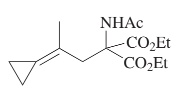
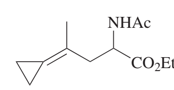
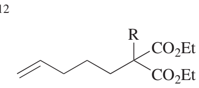
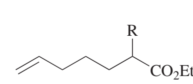
R^1	R^2	R^3	R^4	Config.	Additive	Time (h)		Refs.
Me	H	Me	Me	(*E,Z*)	LiCl	2	(80)	796
Et	Me	Me	Me	(*E*)	NaCl	20	(72)	797
Et	Me	CD_3	Et	(*E,Z*)	LiCl	4	(78)	620

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaBr,[e] 190°, 5 h		798

R^1	R^2	R^3	R^4	R^5	
H	H	Cl	H	*i*-Pr	(—)
H	Cl	H	H	*i*-Pr	(—)
H	Cl	Cl	H	*i*-Pr	(—)
Cl	Cl	H	H	*i*-Pr	(—)
Cl	Cl	H	H	*c*-Pr	(—)
Cl	Cl	H	Me	*c*-Pr	(80)
Cl	Cl	H	H	*s*-Bu	(—)
Cl	Cl	H	H	*i*-Bu	(—)
Cl	Cl	H	H	*t*-Bu	(—)
Cl	Cl	H	H	*c*-C_5H_9	(—)
Cl	Cl	Cl	H	*i*-Pr	(—)
Cl	Cl	Me	H	*i*-Pr	(—)
Br	Br	H	H	Et	(—)
Br	Br	H	H	*i*-Pr	(—)

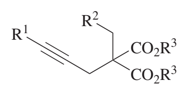
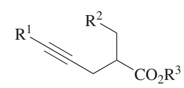
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 	See table.		

n	R	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
1	Me	DMSO	H_2O, NaCl	180	5–10	(67)	776
1	Me	[bmim]Br	LiCl	160	24	(47)	115
1	Et	DMSO	LiCl	reflux	6	(80)	799, 800
1	Et	DMSO	H_2O, LiCl	reflux	6	(86)	801, 802
1	Et	DMSO	H_2O, NaCl	170–180	6	(60–80)	367, 803
1	Et	DMSO	NaCN	160	6	(82)	804, 805, 806
1	Et	[bmim]Br	LiCl	160	24	(51)	115
2	Me	DMSO	H_2O, NaCl	180	overnight	(77)	807, 751

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, H_2O, NaCl, 165°, 8 h	 (73)	143
C_{9-12} 	DMSO, H_2O, additive		

R	Additive	Temp (°)	Time (h)		Refs.
Me	NaCl	189	—	(0)	808
n-Pr	LiCl	180	8–12	(90)	809
n-Bu	LiCl	180	8–12	(86)	809

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-16} 	DMSO, H_2O, additive		

R^1	R^2	R^3	Additive	Temp (°)	Time (h)		Refs.
H	CH≡C	Me	LiCl	reflux	1	(90)	810, 811
H	CH≡C	Me	NaCl	170	15	(—)	812
H	CH≡C	Et	LiCl	reflux	5	(82)	813, 814
H	*n*-Bu	Et	LiCl	185	12	(70)	815
H	Ph	Me	NaCl	150	12	(82)	816
H	(*E*)-4-$MeOC_6H_4CH$=CH	Et	NaCl	reflux	17	(31)	817
H	(*E*)-4-$CF_3C_6H_4CH$=CH	Et	NaCl	reflux	17	(48)	817
TMS	*n*-C_7H_{15}	Et	LiCl	—	—	(0)	818
Et	H	Et	LiCl	reflux	—	(75)	819

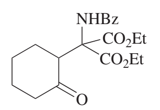
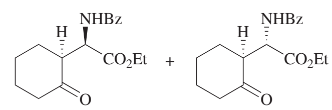
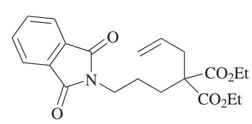
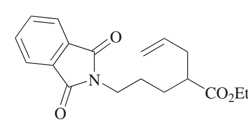
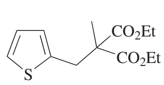
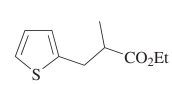
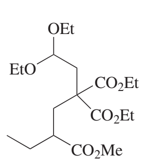
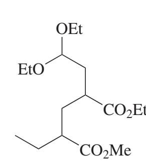
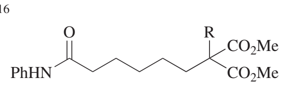
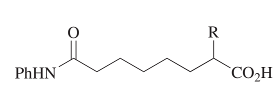
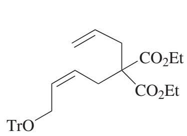
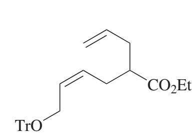
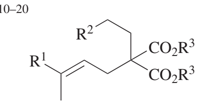
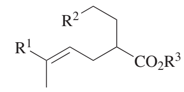
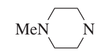
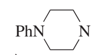
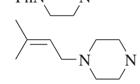
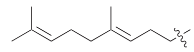
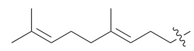
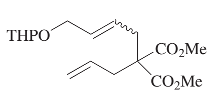
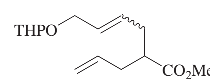
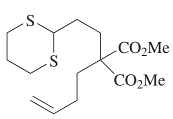
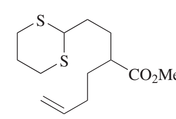
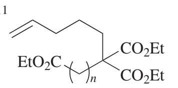
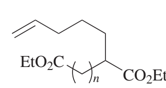
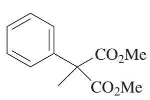
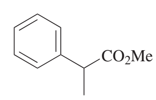
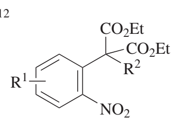
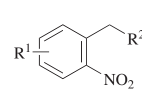
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, H_2O, LiCl, 125°, 6 h	 **I** **II** **I** + **II** (86), **I**/**II** = 4:3[f]	820
	DMSO, H_2O, LiBr, reflux, 40 h	 (—)	821, 822
	DMSO, NaCl	 (—)	823
C_{10} 	DMSO, NaCN, 160°, 4–5 h	 (73)	824, 825
C_{10-16} 	1. DMSO, H_2O, LiCl, reflux 2. NaOH, MeOH, reflux	 (67–83) R: Me, Et, *n*-Pr, allyl, propargyl, *n*-Bu, Bn	826
C_{10} 	DMSO, H_2O, NaCN, 150°, 5 h	 (64)	827

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

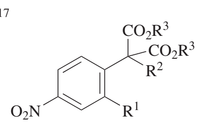
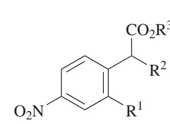
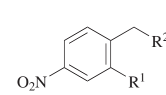
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-20} 	DMSO, NaCN, 160°, 3 h		828

R^1	R^2	R^3	
Me	Me_2N	Et	(66)
Me		Et	(47)
Me		Et	(—)
Me		Et	(50)
	Me_2N	Me	(95)
	Me_2N	Et	(74)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	DMSO, H_2O, NaCl, 160°	 (—)	829
	DMF, NaCN, 120°	 (88)	830, 253

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11} 	DMSO, H_2O, NaBr	 *n*: 1 (77); 2 (98)	831
C_{10} 	$EtCO_2H$, reflux, 72 h	 (0)	322
C_{10-12} 	DMA, MgCl•6H_2O, reflux		518

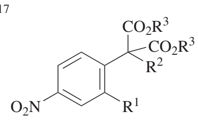
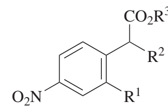
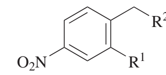
R^1	R^2	Time (h)	[b]
4-Cl	Me	15	(75)
5-Me	Me	20	(69)
4-Cl	allyl	24	(45)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-17} 	See table.	 I +  II	

Continued on next page.

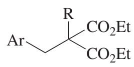
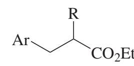
R^1	R^2	R^3	Solvent	Additive(s)	Temp (°)	Time	I	II	Refs.
H	allyl	Me	DMSO	H_2O[g], NaCl	155	overnight[i]	(—)	(61)	146
F	$NC(CH_2)_2$	Me	DMSO	NaCl	155	overnight	(—)	(65)	833
F	$MeO_2C(CH_2)_2$	Me	DMSO	H_2O, NaCl	155	overnight	(38)	(48)	833
Cl	Me	Et	DMA	$MgCl_2$•6H_2O	reflux	15 h	(—)	(72)[b]	518
Cl	EtO_2CCH_2	Me	DMSO	H_2O[g], NaCl	155[h]	overnight[i]	(—)	(61)	146
Cl	$NC(CH_2)_2$	Me	DMSO	H_2O[g], NaCl	155[h]	overnight[i]	(—)	(70)	146
Cl	allyl	Me	DMSO	H_2O[g], NaCl	155[h]	overnight[i]	(—)	(74)	146
Cl	*n*-Bu	Me	DMSO	H_2O[g], NaCl	155[h]	overnight[i]	(0)[j]	(0)	146
Cl	$MeO_2C(CH_2)_2$	Me	DMSO	H_2O[g], NaCl	155[h]	overnight[i]	(10)	(48)	146
Cl	$MeCO(CH_2)_2$	Me	DMSO	H_2O[g], NaCl	110	—	(70)	(—)	146
Cl	$MeCO(CH_2)_2$	Me	DMSO	H_2O[g], NaCl	155	overnight[i]	(—)	(56)	146

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α-DISUBSTITUTED MALONATES (*Continued*)

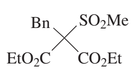
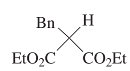
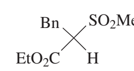
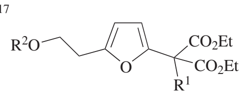
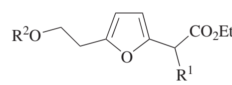
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-17} 	See table.	 I +  II	

Continued from previous page.

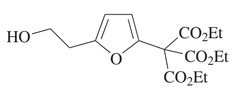
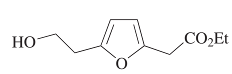
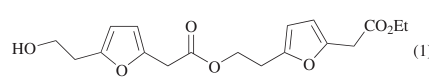
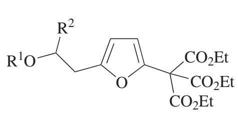
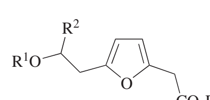
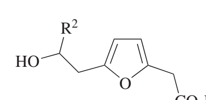
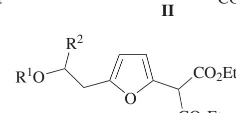
R^1	R^2	R^3	Solvent	Additive(s)	Temp (º)	Time	I	II	Refs.
Cl	(*E*)-$EtO_2CCH{=}CHCH_2$	Me	DMSO	H_2O^g, NaCl	155^h	overnight[i]	(10)	(44)	146
Cl	Bn	Me	DMSO	H_2O^g, NaCl	110	—	(73)	(—)	146
Cl	Bn	Me	DMSO	H_2O, NaCl	155	overnight	(—)	(85)	146
Cl	$BzCH_2$	Me	DMSO	H_2O^g, NaCl	155^h	overnight[i]	(—)	(56)	146

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	See table.		

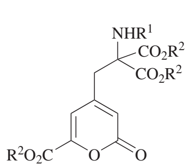
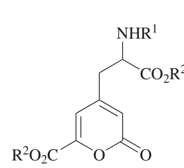
Ar	R	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
Ph	Me_2N	DMSO	NaCN	—	—	(—)	834
2,3,4,5,6-F_5C_6	AcHN	DMF	H_2O, LiBr	reflux	4.5	(73)	835
3-$PhOC_6H_4$	AcHN	DMF	H_2O, LiBr	138	16	(85)	836

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhH, DABCO, reflux, 8 h	 (48) +  (52)	837
C_{10-17} 	DMSO, H_2O, LiCl		144

R^1	R^2	Temp (º)	Time (h)	
Me	Bn	190	2	(91)
Bn	Bn	190	2	(65)
n-C_8H_{17}	H	160	3.5	(56)
n-C_8H_{17}	Bn	190	2	(73)

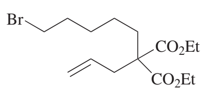
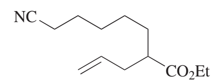
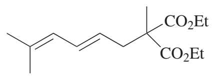
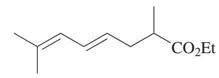
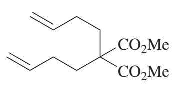
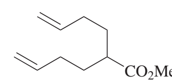
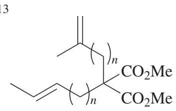
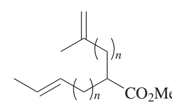
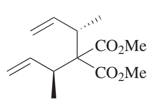
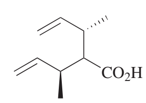
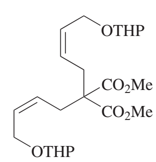
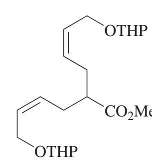
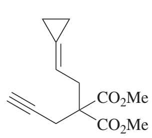
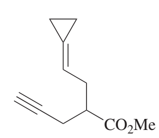
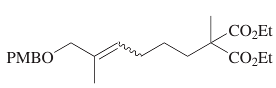
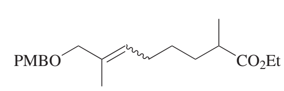
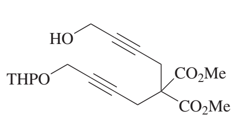
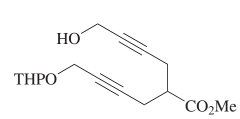
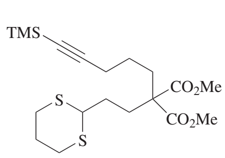
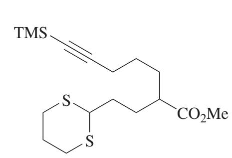
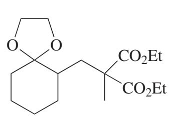
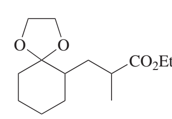
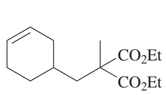
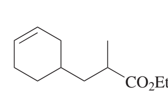
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	DMSO, H_2O, LiCl, 190°, 2 h	 (19) +  (1)	144
	DMSO, H_2O, LiCl, 2 h	 I +  II +  III	144

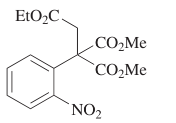
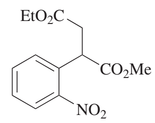
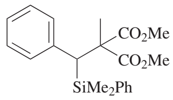
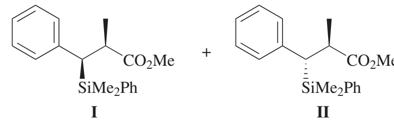
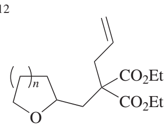
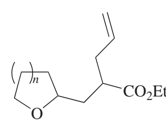
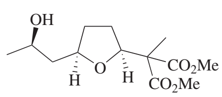
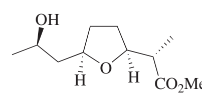
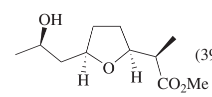
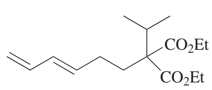
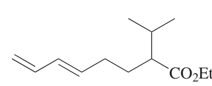
R^1	R^2	Temp (º)	I	II	III
Ac	H	160	(32)	(0)	(17)
Ac	H	190	(4)	(14)	(0)
Bn	H	190	(67–80)	(0)	(0)
Bn	Me	190	(63)	(0)	(0)

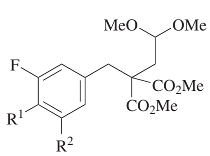
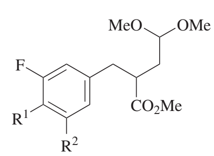
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	See table.		123

R^1	R^2	Solvent	Additive	Temp (º)	Time (h)	
Ac	Me	DMF	CF_3CO_2K	110–120	5	(63)
Ac	Et	HMPA	$Me_4N^+AcO^-$	75–80	13	(16)
CF_3CO	Me	DMF	CF_3CO_2K	110–120	3	(32)

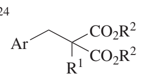
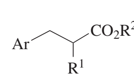
TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMSO, NaCN	 (60)	149
	DMSO, H_2O, NaCN, 170°, 5 h	 (82)	487
	DMSO, H_2O, NaCl, 180°, 4 h	 (90)	776
$C_{11–13}$			
	DMSO, H_2O, NaCl, 185°, overnight	 *n* — 1 (69); 2 (83)	807
C_{11}			
	DMSO, KCN, 140°, 43 h	 (93)	838
	DMSO, H_2O, KOAc, 140°, 5 h	 (81)	404, 405
	DMSO, NaCN, 120°, 4 h	 (62)	839
	DMSO, H_2O, NaCN, 145°, 6 h	 Config. — (*E*) (60); (*Z*) (—)	840
	DMSO, NaCN, 100°, 1.75 h	 (58)	403, 841
	DMSO, NaCN, 120°, 16 h	 (64)	842
	DMSO, H_2O, LiCl, reflux, 6 h	 (65)	832
	DMSO, H_2O, LiCl, reflux, 21.5 h	 (88)	843

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMSO, H_2O^g, NaCl, 110°	 (58)	146
	DMSO, H_2O, LiCl, reflux, 25 min	 **I + II** (68), **I/II** = 70:30	25
$C_{11–12}$			
	DMSO, H_2O, LiCl, 195°, 2 h	 *n* 1 (—) 2 (—)	844
C_{11}			
	DMSO, H_2O, NaCl, reflux, 3 h	 (39) +  (39)	244
C_{12}			
	DMSO, H_2O, LiCl, 180°, 6 h	 (54)	845, 846

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 180°, overnight		847

R^1	R^2	
H	H	(20)
H	F	(25)
MeO	H	(23)
MeO	F	(24)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{12–24}$			
	DMSO, additive(s)		

Ar	R^1	R^2	Additive(s)	Temp (°)	Time (h)		Refs.
4-ClC_6H_4	*i*-Pr	Et	H_2O, KOAc	reflux	—	(50)	548
3-IC_6H_4	Et	Et	H_2O, NaCl	170	6	(74)	848
2-IC_6H_4	$BzCH_2$	Me	H_2O, NaCl	155	10	(40)	849
3-$MeOC_6H_4$	Et	Et	H_2O, LiCl	180	—	(84)	850
3-$MeOC_6H_4$	*n*-Pr	Et	H_2O, LiCl	180	—	(89)	850
4-*t*-BuC_6H_4	Me	Et	NaCN	160–170	4.5	(85)	851
1-naphthyl	$Ph(CH_2)_4$	Et	H_2O, LiCl	180–190	8	(90)	852

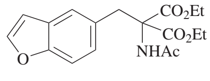
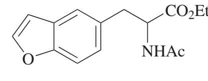
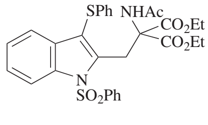
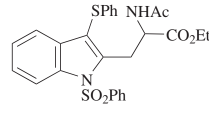
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	DMF, H_2O, LiCl, 140°, 16 h	 (79)	853
	DMSO, H_2O, NaCl, 180–190°, 3 h	 (95)	854

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

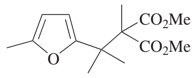
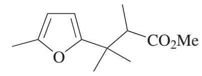
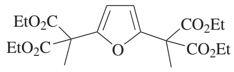
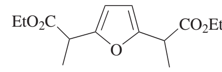
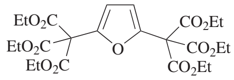
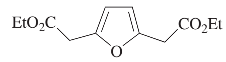
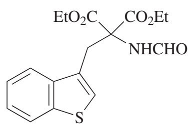
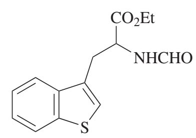
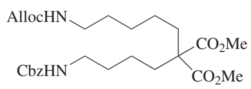
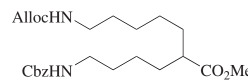
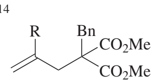
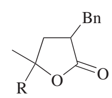
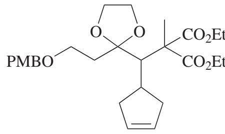
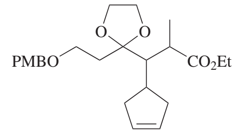
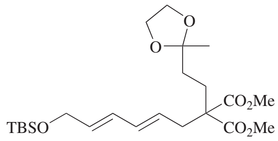
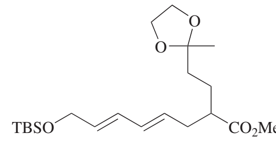
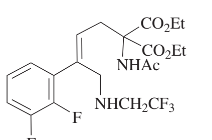
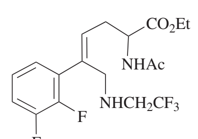
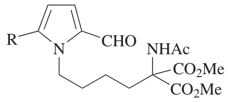
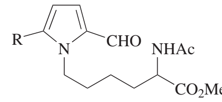
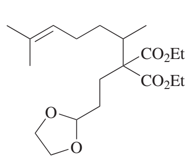
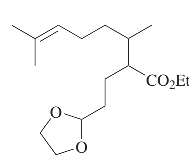
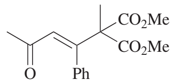
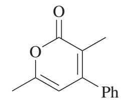
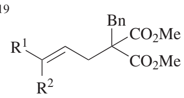
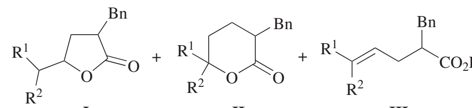
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	DMF, LiI, reflux, 5 h	 (63)	598
	DMSO, H_2O, LiCl, 190°, 2 h	 (25)	144
	DMSO, H_2O, LiCl, 2 h	 (23)	144
	DMSO, H_2O, NaCl, 200°, 15 min	 (53)	855
C_{13} 	DMSO, H_2O, LiCl, 160°, 4 h	 (66)	856
$C_{13–14}$ 	[Bmim]Br/[bmim]BF_4 (1:1), H_2O, LiCl, 160°, 24 h	 R / dr; H (89) 1.3:1; Me (93) —	115
C_{13} 	DMSO, NaCN, 180°, 4 h	 (76)	857
	DMF, H_2O, LiCl, 160°, 2.5 h	 (61)	858
	DMA, H_2O, LiCl, 113–115°, 12–14 h	 (96)	859, 860
	DMSO, LiI•$2H_2O$, 120°, 4 h	 R; CHO (—); $HOCH_2$ (—)	861
C_{14} 	DMSO, H_2O, NaCl, 180–185°, 8 h	 (60)	862

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	DMSO, H_2O, LiCl or NaCl or KCl, reflux, 1 h	 (55)	174
C_{14-19}			
	[Bmim]Br/[bmim]BF_4 (1:1), H_2O, LiCl, 160°, 24 h	 **I** + **II** + **III**	115

R^1	R^2	**I**	**I** dr	**II**	**II** dr	**III**
H	Me[k]	(49)	1:1	(34)	1.9:1	(0)
Me	Me	(45)	1.3:1	(45)	—	(0)
Ph	H	(15)	1.3:1	(0)	—	(80)

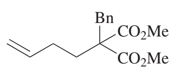
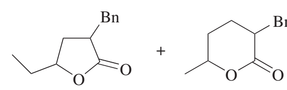
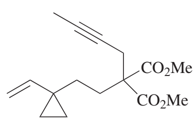
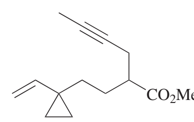
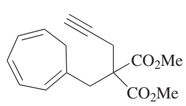
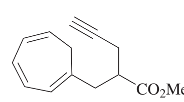
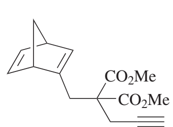
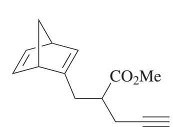
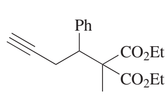
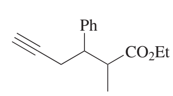
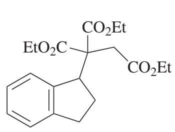
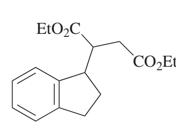
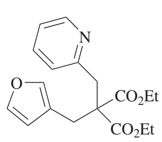
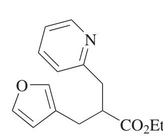
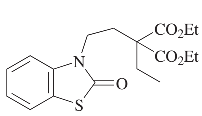
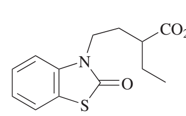
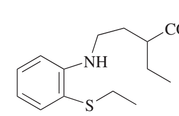
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	[Bmim]Br/[bmim]BF_4 (1:1), H_2O, LiCl, 160°, 24 h	 (55) 1.1:1 dr + (5) 1.7:1 dr	115
	DMF, LiCl, Ar, 150°, 2.5 h	 (88)	863
	DMSO, H_2O, HI, 90°, 4 h	 (65)	864
	DMSO, NaI, 100°, 5 d	 (49)	865
	DMSO, H_2O, NaCl, 160–170°, 2 d	 (92) 1:1 dr	866
	DMSO, H_2O, NaCl, 178–183°, 6 h	 (85)	867
	DMSO, H_2O, LiCl, reflux, 2 h	 (—)	868
	DMSO, H_2O, KCN, reflux, 12 h	 (75) +  (25)	869

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

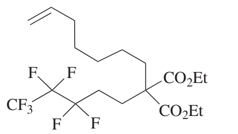
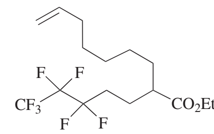
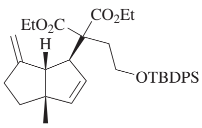
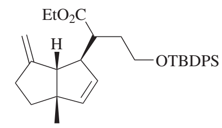
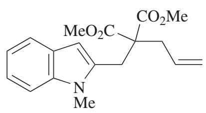
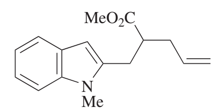
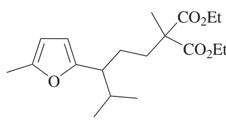
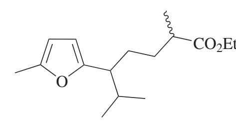
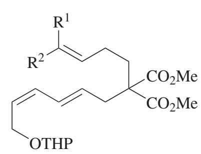
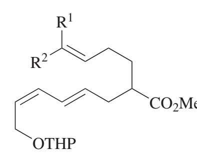
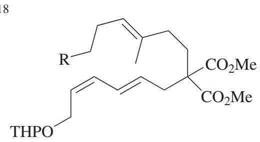
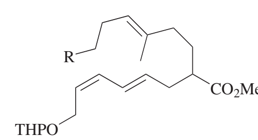
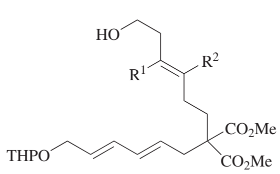
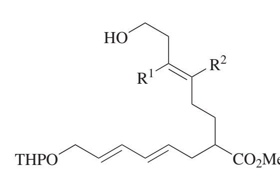
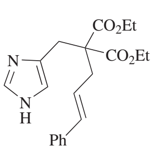
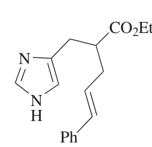
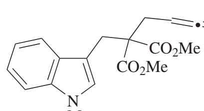
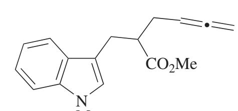
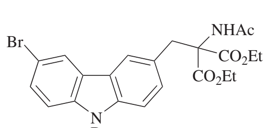
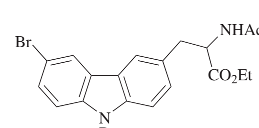
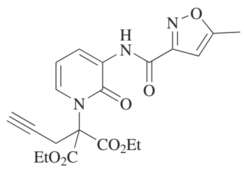
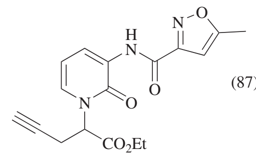
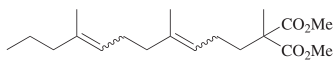
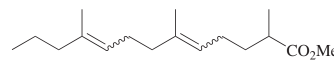
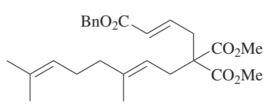
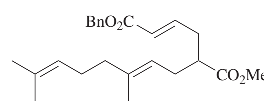
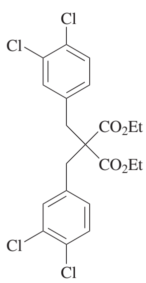
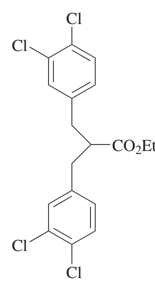
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	DMSO, H_2O, LiCl, 170–180°, 5 h	 (89)	870
	DMSO, H_2O, LiCl, reflux, 6 h	 (84)	148
	DMSO, H_2O, NaCl, reflux, 2 h	 (73)	871
	DMSO, H_2O, LiCl, 180°, 4 h	 (81)	872
C_{16}			
	DMSO, H_2O, NaCN, 95°	 R^1 / R^2 / Time (h): Me / $HO(CH_2)_2$ / 37 (88); $HO(CH_2)_2$ / Me / 30 (81)	873, 874
$C_{16–18}$			
	DMSO, H_2O, NaCN, 95°	 R / Time (h): HO / 39 (85); MeO_2CCH_2 / 35 (69)	874
C_{16}			
	DMSO, H_2O, NaCN, 95°, 48 h	 R^1 / R^2: H / Me (77); Me / H (72)	875
	DMSO, H_2O, NaCN, 120°, 48 h	 (45)	876
	DMSO, H_2O, NaCl, reflux, 2 h	 (70)	877
	DMSO, H_2O, LiCl, reflux, 1.75 h	 (70)	878, 879

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α-DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	DMA, LiBr, 85°, 16 h	 (87)	880
C_{17}			
	DMSO, H_2O, NaCl, 190°, 12 h	 (85)[b]	881
	DMF, H_2O, Mw, 160°, 20 min	 (—)[l]	17
	*o*-Xylene, base, reflux		

Base	Time (h)		Refs.
DABCO	4	(79)	291
DBN	1.5	(96)	291
3-quinuclidinol	6	(93)	291
perloline HCl	18	(89)	882
quinine monohydrate	25	(85)	882
quinidine	24	(4)	883
brucine	24	(17)	883
tropine	24	(6)	883
nicotine	24	(2)	883
reserpine	24	(0.2)	883
yohimbine HCl	24	(0.2)	883

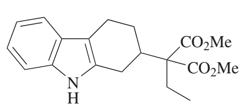
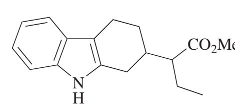
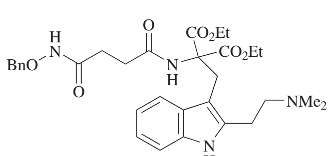
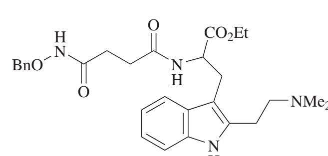
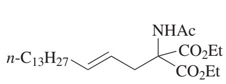
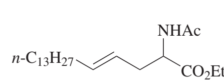
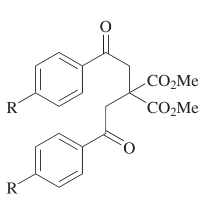
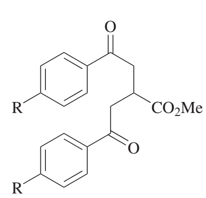
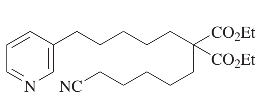
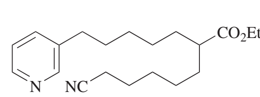
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 160–170°, 18 h	 (53)	884
C_{18}			
	Krapcho	 (0)	885
C_{19}			
	DMSO, H_2O, NaCl, reflux, 18 h	 (82)	886
	DMSO, H_2O, NaCl, 130–150°, 2.5 h	 R: H (69); Cl (68); MeO (66)	887
	DMSO, H_2O, NaCl, "heat"	 (—)	888

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

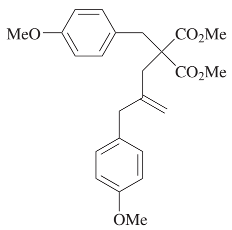
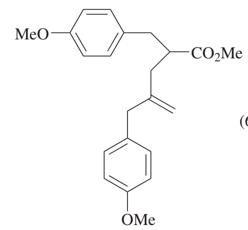
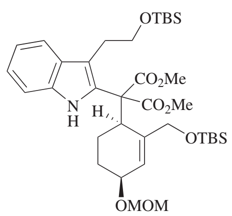
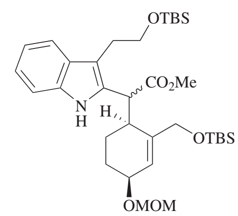
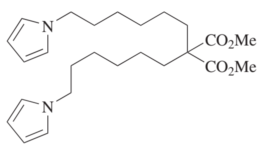
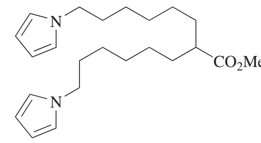
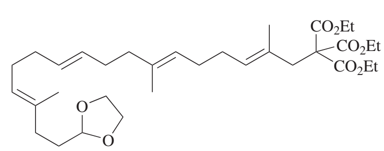
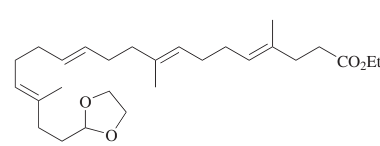
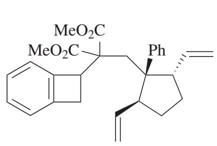
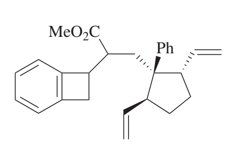
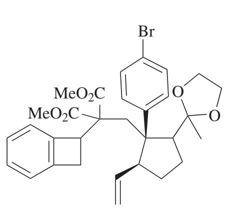
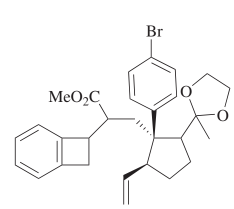
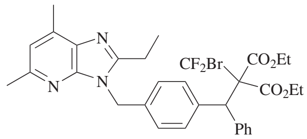
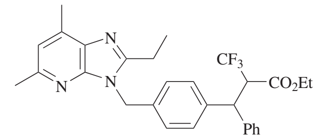
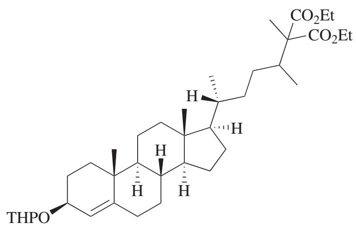
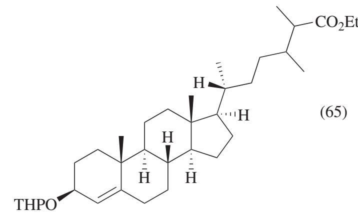
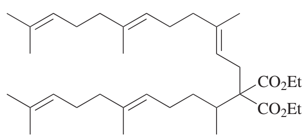
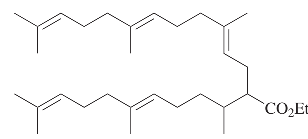
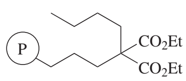
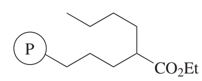
Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	DMSO, H_2O, NaCl, 195°, 3 h	 (60)	889, 890
	Collidine, LiI, 80°, 1 h	 (—)	891
C_{23}			
	DMSO, H_2O, NaCN, 145°, 20 min	 (56)	892
C_{25}			
	DMSO, H_2O, LiCl, 189°, 8 h	 (64)	142
C_{27}			
	DMSO, H_2O, NaCN, 90°, 22 h	 (84) 4 diastereomers	893
	DMSO, H_2O, NaCN, 90°, 15 h	 (78) mixture of diastereomers	894
C_{28}			
	DMSO, KF, 170°, 2 h	 (23)	895

TABLE 3. DEALKOXYCARBONYLATIONS OF α,α–DISUBSTITUTED MALONATES (*Continued*)

Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29} 	DMSO, NaCN, 160°, 10 h	 (65)	896
C_{31} 	DMSO, NaCN, 180°, 5 h	 (73)	897
C_n  P = 2% crosslinked styrene–divinylbenzene copolymer	See table.		898

Solvent	Additive	Temp (°)	
DMSO	NaI	100	(100)
DMSO	$CaCl_2$	100	(100)
$MeNO_2$	NaI	—	(—)

[a] The number is the percent conversion.

[b] The yield includes that of the preparation of the substrate.

[c] The preparation of the substrate by reaction of $R^1R^2BrCNO_2$ with the sodium salt of the requisite R^3-substituted diethyl malonate and the subsequent dealkoxycarbonylations were carried out in one pot; the yield is for both reactions.

[d] The substrate has carbon-13 in the 2-position.

[e] The reaction was slower when NaCl was used.

[f] The *syn*-isomer was obtained in 44% yield by fractional crystallization.

[g] The authors do not state that water was added but the single experimental procedure uses 4% water in DMSO.

[h] The temperature was not given but a number of experiments that led to complete dealkoxycarbonylation were carried out at 155°.

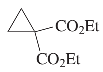
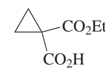
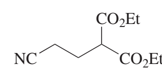
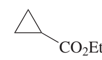
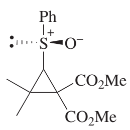
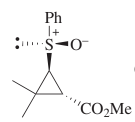
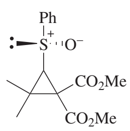
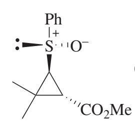
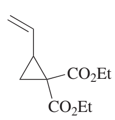
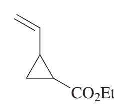
[i] No time was given but the single experimental procedure lists it as "overnight".

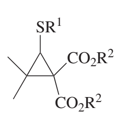
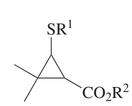
[j] The starting material was recovered.

[k] The substrate was a 5:1 mixture of (*E*) and (*Z*) isomers.

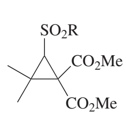
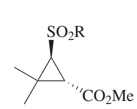
[l] The product was a mixture of unreacted substrate and decomposition products.

TABLE 4A. DEALKOXYCARBONYLATIONS OF THREE-MEMBERED CYCLIC GEMINAL DIESTERS

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	PhMe, MgI_2, reflux	 (58)	899
	HMPA, NaCN, 150°, 10 min	 (54)	150
	$PhCO_2H$, (n-Bu)$_4$NBr, 200°, 4 h	 (0)[a]	321
C_7 	DMSO, H_2O, NaCl, reflux, 4 h	 (70)	256
	DMSO, H_2O, NaCl, reflux, 4 h	 (70)	256
	DMSO, NaCN, reflux	 (0)	151

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	See table.		

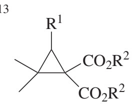
R^1	R^2	Solvent	Additives	Temp	Time (h)		*trans/cis*	Refs.
Me	Et	1-oxo-1-methylphospholine	H_2O, NaBr	156º	12	(69)	—	113
Et	Me	DMSO	H_2O, NaCl	reflux	5	(86)	62:38	249
$HO(CH_2)_2$	Me	DMSO	H_2O, NaCl	reflux	5	(58)	79:21	249
Ph	Me	DMSO	H_2O, NaCl	reflux	—	(94)	mixture	901, 902
Ph	Et	DMSO	H_2O, NaCl	reflux	5	(75)	67:33	249
2-$MeOC_6H_4$	Me	DMSO	H_2O, NaCl	reflux	5	(79)	65:35	249
2-$MeO_2CC_6H_4$	Me	DMSO	H_2O, NaCl	reflux	5	(60)	68:32	249
Bn	Me	DMSO	H_2O, NaCl	reflux	5	(88)	65:35	249

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, reflux, 2 h		249

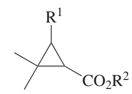
R	
Et	(68)
$HO(CH_2)_2$	(47)
Ph	(72)
2-MeC_6H_4	(74)
4-MeC_6H_4	(75)
Bn	(95)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{7-13}

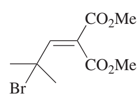


See table.

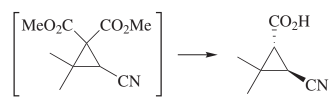


R^1	R^2	Solvent	Additive(s)	Temp (°)	Time (h)		*trans/cis*	Refs.
PhO	Me	DMSO	H_2O, NaCl	165	6	(40)	100:0	27
MeO_2C	Me	DMF	H_2O, NaCl	150	48	(84)	—	903
Cl_2C=CH	Et	DMSO	H_2O, NaCl	175	9	(15–20)	—	112, 113
Cl_2C=CH	Et	1-oxo-1-methylphospholine	H_2O, NaCl	175	10	(77)	—	113
(*E*)-CF_3CH=CH	Me	DMSO	NaCN	160	1.5	(47)	50:50	904
MeC≡C	Et	1-oxo-1-ethyl-3-methylphospholine	H_2O, Et_4NCl	180	12	(75)	—	113
MeC≡C	Et	DMSO	H_2O, NaCl	180	12	(25)	—	113
Me_2C=CH	Me	—	—	—	—	—	—	905
4-$MeOC_6H_4$	Et	DMSO	KCN	160	48	(51)	100:0	906, 907[b]

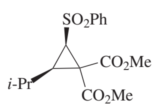
C_8



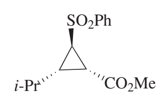
1. DMSO, NaCN, rt, 3 h
2. 80°, 3 h



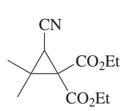
(67) — 900



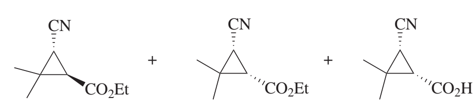
DMSO, H_2O, NaCl, reflux, 4 h



(89) — 27



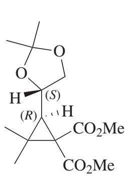
See table.



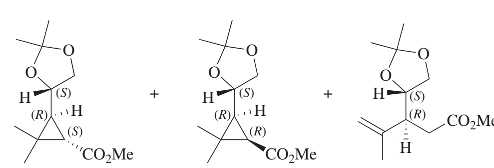
I II III

Solvent	Additive(s)	Temp (°)	Time (h)	I	II	III	Refs.
1-oxo-1-ethyl-3-methylphospholine	H_2O, NaBr	180	12	(—)	(—)	(0)	113
DMSO	NaCN	175	2.5	(8)	(9)	(44)	250
DMSO	H_2O, NaCN	—	—	(0)	(0)	"only"	250

C_9

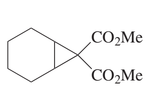


See table.

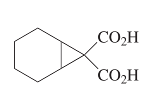


I II III — 117

Solvent	Additives	Temp (°)	Time (h)	I + II + III	I/II/III
DMSO	H_2O, NaCl	160	6	(73)	27:21:52
DMF	H_2O, NaCN	120	48	(88)	50:34:16
DMF	Cs_2CO_3, 4-$H_2NC_6H_4SH$	90	26	(68)	61:39:0
DMPU	$Me_4N^+AcO^-$	95	4	(90)	70:30:0

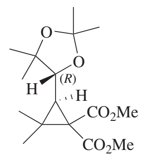
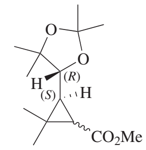
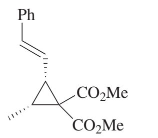
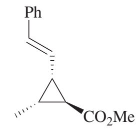
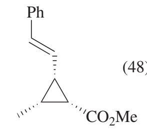
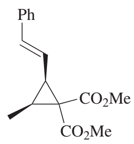
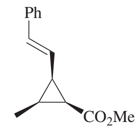
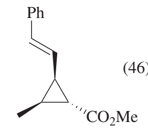
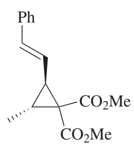
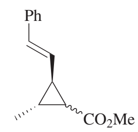
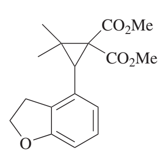
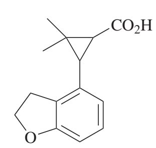
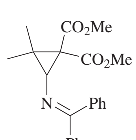
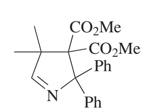


DMF, KCN, reflux, 12 h



(65) — 167

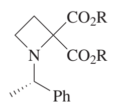
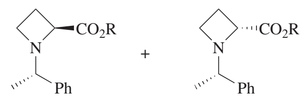
TABLE 4A. DEALKOXYCARBONYLATIONS OF THREE-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	HMPA, $Me_4N^+AcO^-$, 95°, 6 h	 (74) *trans*/*cis* = 81:19	117
C_{14} 	DMSO, H_2O, LiCl, 195°, 4 h	 (48) +  (48)	152
	DMSO, H_2O, LiCl, 195°, 4 h	 (46) +  (46)	152
	DMSO, H_2O, LiCl, 195°, 4 h	 (85) unseparable mixture	152
C_{15} 	DMSO, NaCN, 150°, 23 h	 (—) *trans*/*cis* = 9:1	908
C_{20} 	DMSO, H_2O, NaCl, "heat", 23 h	 (67)	153

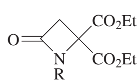
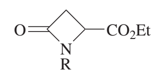
[a] The reference reported "no reaction".

[b] A small amount of the *cis*-ester was isolated.

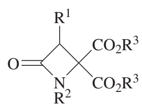
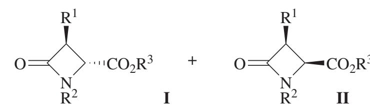
TABLE 4B. DEALKOXYCARBONYLATIONS OF FOUR-MEMBERED CYCLIC GEMINAL DIESTERS

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	DMSO, additives	 I + II	35

R	Additives	Temp (°)	Time	I + II	I/II[a]
Me	H_2O, NaCl	160	—	(65)	—
Me	2,6-(t-Bu)$_2$-4-MeC_6H_2OH, LiCl, 3 Å MS	140	2 h	(78)	2.7:1
Me	(S)-binaphthol, LiCl, 3 Å MS	—	—	(23)	2.8:1
Et	H_2O, NaCl	160	—[b]	(—)	—

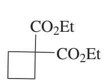
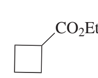
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 170–180°, 5 h		154

R	
H	(0)
$EtO_2C(CH_2)_2$	(43)
Ph	(94)
Bn	(75)
2,4-$(MeO)_2C_6H_3CH_2$	(90)
3,4-$(MeO)_2C_6H_3CH_2$	(81)

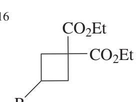
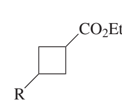
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{5–8}$ 	See table.	 I + II	

R¹	R²	R³	Solvent	Additive(s)	Temp (°)	Time	I + II	I/II	Refs.
H	PNP	Et	DMSO	H_2O, NaCl	177–180	—	(52)	—	909
H	PMB	Et	DMSO	H_2O, NaCl	180	8 h	(90)	—	910, 911
PhO	PMP	Et	DMF	LiCl	Mw, 140	7–8 min	(64)	1:1	30
PhS	PMP	Et	DMSO	H_2O, NaCl	reflux	4 h	(81)	1:12	31

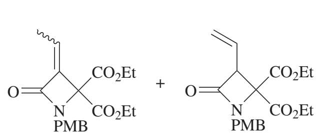
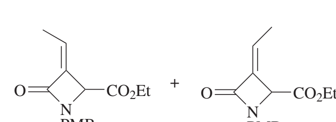
R¹	R²	R³	Solvent	Additive(s)	Temp (°)	Time	I + II	I/II	Refs.
BnO	PMP	Et	DMF	LiCl	Mw, 140	7–8 min	(79)	2:1	30
Me	DMB	Et	DMSO	H_2O, NaCl	170–180	30 h	(87)	—	912
Et	DMB	Me	DMSO	H_2O, NaCl	180	9 h	(90)	mixture	913, 914
i-Pr	DMB	Me	DMSO	H_2O, NaCl	170–180	—	(85)	9:1	32, 915
i-Pr	DMB	Et	DMSO	H_2O, NaCl	170–180	—	(76)	9:1	32, 915
i-Pr	DMB	Et	DMSO	H_2O, NaCl	180	—	(100)	mixture	913, 914

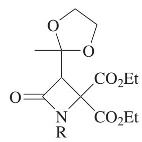
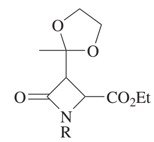
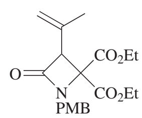
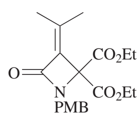
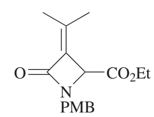
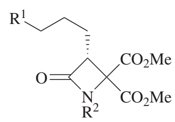
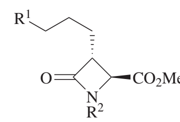
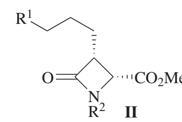
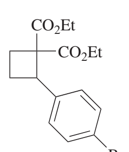
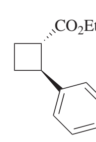
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	See table.		

Solvent	Additive(s)	Temp	Time (h)		Refs.
DMSO	NaCN	160°	4	(75)	108
$(n\text{-}Bu)_2SO$	NaCN	160°; then distill	4	(65)	108
EtOH, dioxane	KOH, 18-c-6	rt; then reflux	0.5; 40	(76)	330

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{6–16}$ 	DMSO, H_2O, additive		

R	Additive	Temp (°)	Time (h)		$trans/cis$	Refs.
BnO	NaCl	210	48	(88)	57:43	156
4-t-BuC_6H_4	LiCl	140–150	12	(70)	—	916

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7  75:25	DMF, LiCl, Mw, 140°, 7–8 min	 (—) 1:1	30, 917

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	DMSO, H_2O, NaCl, 175°		918
C_8  +  75:25	DMF, LiCl, Mw, 140°, 7–8 min	 (80)	30, 919, 917
 x [M]	DMF, H_2O, LiCl, 130°	 I +  II	33
C_{12} 	DMSO, H_2O, LiCl, reflux, 4 h	 (72)	155

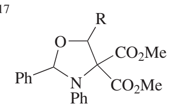
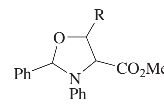
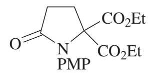
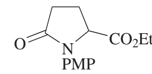
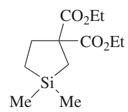
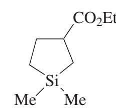
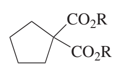
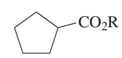
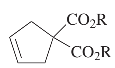
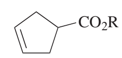
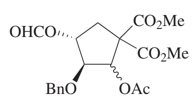
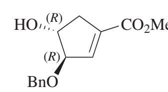
R	
Ph	(71)
PMB	(66)
Bn	(—)
3,4-$(MeO)_2C_6H_3CH_2$	(80)

R^1	R^2	x	Time (h)	**I + II**	**I/II**
CF_3CONH	H	0.15	—	(—)	9:1
CF_3CONH	DMB	0.25	3.5	(93)	36.3:1
CF_3CONH	DMB	0.09	—	(—)	46:1
CbzNH	DMB	0.09	—	(—)	25:1
PhthN	DMB	0.09	—	(—)	1.25:1

[a] Treatment of isomer **II** with LDA in THF followed by protonation with aq NH_4Cl at –78° produced a 6.7:1 mixture of **I** and **II**. The two diastereomers did not interconvert by the action of NaOMe or DBU in refluxing MeOH.

[b] The reaction was reported to be very slow.

TABLE 4C. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC GEMINAL DIESTERS

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-17} 	PhMe, piperidine, heat	 R Me (—) Ph_2CH (—)	920
C_6 	DMSO-d_6, H_2O, NaCl, 185–190°, 24 h	 (82)	921
	DMSO, LiCl, heat	 (32–80)	922
C_7 	See table.	 R / Solvent / Additive(s) / Temp / Time (h) Et / DMSO / NaCN / 160° / 6 / (80) 108 Et / *o*-xylene / DABCO / reflux / 48 / (73)[a] 291	108, 291
	DMSO, additive	 R / Additive / Temp (°) / Time (h) Me / LiCl / 150 / 3 / (78) 924 Et / NaCN / 160 / 6 / (—) 804 Me / H_2O, LiCl / — / — / (85) 923	924, 804, 923
	1. DMSO, H_2O, NaCl, 125–155°, 3 h; then 155°, 6.5 h 2. MeONa, MeOH	 (65)	925

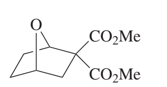
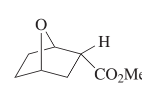
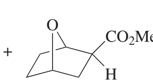
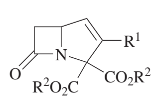
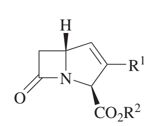
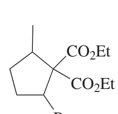
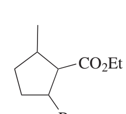
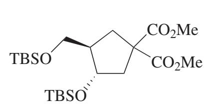
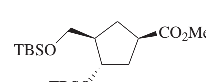
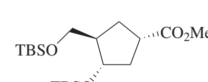
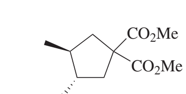
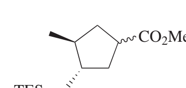
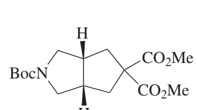
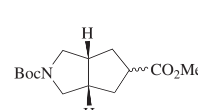
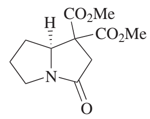
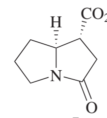
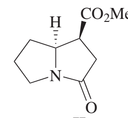
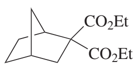
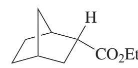
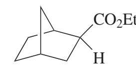
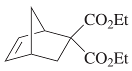
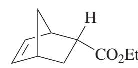
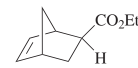
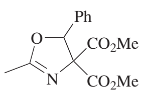
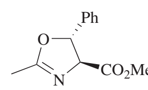
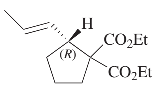
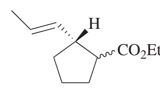
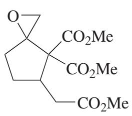
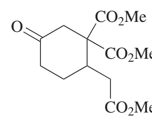
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	DMSO, H_2O, LiCl, 135°, 3–4 h	 **I** +  **II** **I** + **II** (—), **I/II** = 77:23	43
C_{8-9} 	Collidine, LiI	 R^1 / R^2 / Temp (°) / Time MeS / Bn / 120 / 0.5 h / (53) 926 $BzOCH_2$ / PNB / 150 / 20 min / (52) 289	926, 289
	DMSO, H_2O, LiCl, 190°, overnight	 R H (80) Me (78)	927
C_8 	DMSO, H_2O, NaCl, 170°, 8 h	 **I** +  **II** **I** + **II** (89), **I/II** = 1:1	928
C_9 	THF, (n-Bu)$_4$NF, rt, 2 d	 (77)	929
	DMSO, NaCN, 160°	 (63)	930

TABLE 4C. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	DMSO, H_2O, LiCl, reflux to end of gas evolution	 **I** +  **II** **I** + **II** (85), **I/II** = 4:1	931
	DMSO, H_2O, LiCl, 185°, 4 h	 **I** +  **II** **I** + **II** (63), **I/II** = 69:31	42
	DMSO, H_2O, LiCl, 193°, 1 h	 **I** +  **II** **I** + **II** (22), **I/II** = 80:20	42
C_{10}			
	MeCN, piperidine, 81°, 48 h	 (80)	932, 933
	DMSO, H_2O, LiCl	 (—)	934
	LiI, CH_2Cl_2, rt	 (90)	242

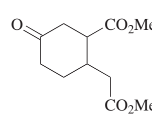
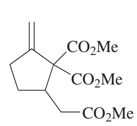
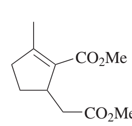
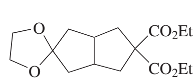
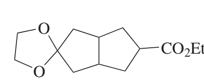
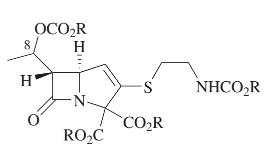
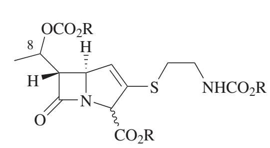
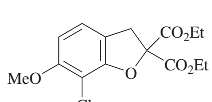
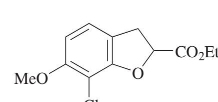
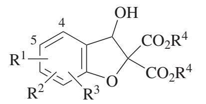
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, LiI, 130°	 (50)	242
	DMSO, H_2O, LiCl, 130°	 (90)	258
	DMSO, H_2O, NaCl, 200°, 24 h	 (76)	935
 R = PNB	2,4,6-Collidine, LiI, 120–130°, 0.5 h	 C-8 Config. (*R*) (45) (*S*) (45)	926, 936
	DMSO, H_2O, LiCl, reflux, 2 h	 (69)	937

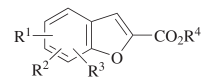
TABLE 4C. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{10}

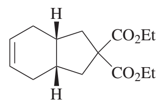


See table.

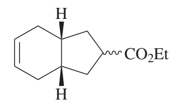


R^1	R^2	R^3	R^4	Solvent	Additives	Temp (º)	Time (h)		Refs.
H	H	H	Et	DMSO	—	reflux	2	(25)	938
H	H	H	Et	—	—	melting at 180–190	2	(50)	938
4-MeO	6-MeO	7-Me	Et	DMSO	H_2O, LiCl	165	1	(86)	939
5-Me	7-Me_2NCH_2	H	Me	DMSO	—	reflux	2	(82)	938
5-Me	7-Me_2NCH_2	H	Me	DMSO	H_2O, NaCl	reflux	2	(60–75)	938
4-*i*-Pr	7-Me	H	Et	DMSO	H_2O, LiCl	165	2	(79)	940

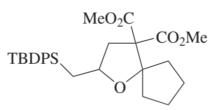
C_{11}



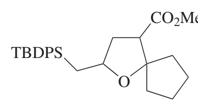
DMSO, NaCN



(—) 941

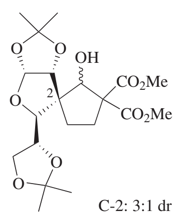


DMSO, H_2O, NaCl, 160–170°, 4 h



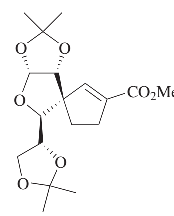
(85) 1:1 dr 159

C_{12}

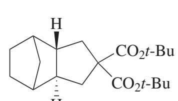


C-2: 3:1 dr

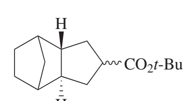
DMSO, H_2O, NaCl, 160°, 4 h



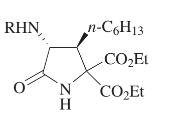
(80) 942



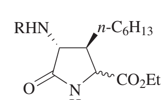
Collidine, LiI•$3H_2O$, reflux, 24 h



(—) 943

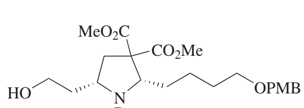


See table.

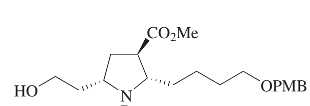


944

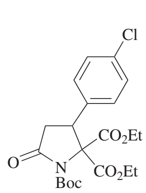
R	Solvent	Additives	Temp (º)	Time (h)		dr
Boc	DMSO	H_2O, NaCl	—	—	(0)	—
Boc	DMEU	H_2O, LiBr	155	4	(64)	1:1
Ts	DMEU	H_2O, LiBr	155	4	(42)	1:1



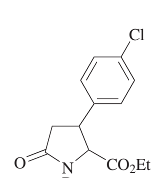
DMSO, H_2O, NaCN, Mw, 140°, 12 min



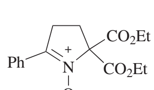
(86)[b] 945



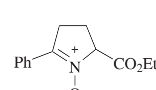
DMSO, H_2O, NaCl, 150°, 40 h



(100) *cis*/*trans* = 2:1 37

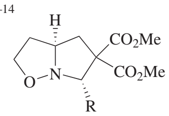
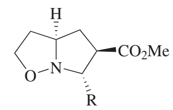
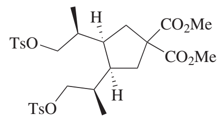
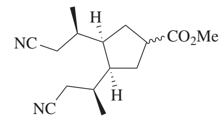
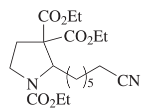
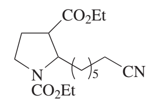
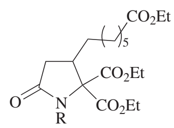
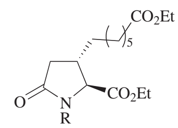
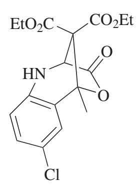
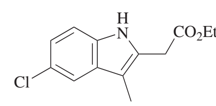
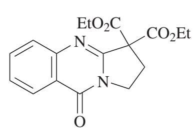
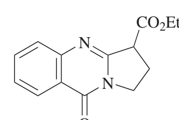
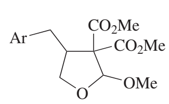
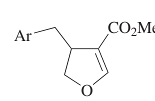
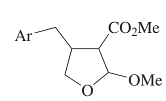


Krapcho



(0) 946

TABLE 4C. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-14} 	DMSO, NaCN, Mw, 145°, 15 min	 R / dr: *t*-Bu (91) 10:0; Ph (89) 10:1.4; 4-BrC$_6$H$_4$ (90) 10:1.5	158
C_{13} 	DMSO, KCN, 90–100°, 12 h	 (50)	947
	DMSO, H$_2$O, NaCl, 175°	 (60) *trans*/*cis* = 5:1	948
	DMSO, H$_2$O, NaCl, reflux, 2 h	 R: H (83); Me (84)	38
	H$_2$O, 180°, 18 h	 (83)	949
	EtOH, NH$_3$, overnight	 (62)	950
	See table.	 I +  II	236

Ar	Solvent	Additive(s)	Temp (°)	Time (min)	I	II	I/II
3,4-(MeO)$_2$C$_6$H$_3$	NMP	TFA, LiCl	Mw, 180	5	(76)	(0)	—
3,4-(OCH$_2$O)C$_6$H$_3$	NMP	TFA, LiCl	Mw, 180	5	(79)	(0)	—
3,4-(OCH$_2$O)C$_6$H$_3$	DMSO	NaCl	130	—	(—)	(—)	1:1

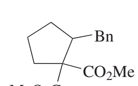
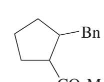
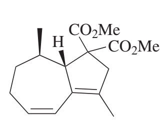
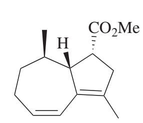
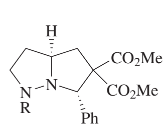
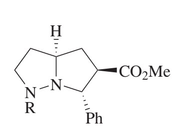
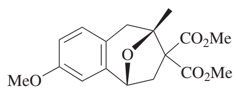
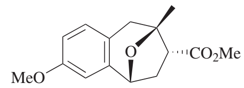
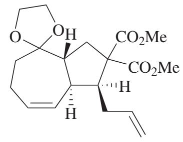
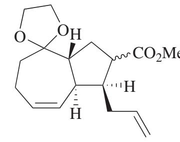
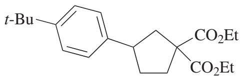
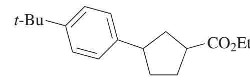
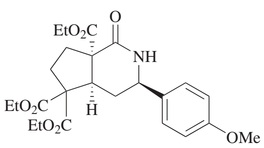
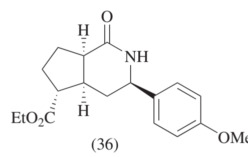
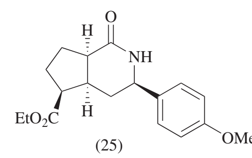
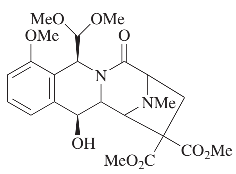
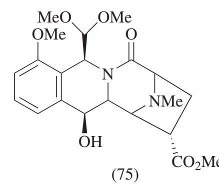
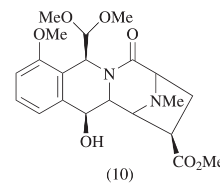
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	DMF, NaCN, reflux, 2.5 h	 (67) 84:16 dr	36
	DMF, NaI, NaHCO$_3$, 160°, 5 h	 (95)	210
	1. DMSO, H$_2$O, NaCN, Mw, 140°, 25 min 2. CH$_2$N$_2$	 R / dr: Boc (98) 10:1; Bz (85) —	951

TABLE 4C. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	DMSO, H_2O, LiCl, 160°, 10 h	 (79) >20:1 dr	67
C_{15} 	DMF, NaI, $NaHCO_3$, 150°	 (99)	952
C_{17} 	DMSO, H_2O, LiCl, reflux, 4 h	 (56)	916
	DMF, H_2O, LiCl, reflux, 18 h	 (36) +  (25)	64
	DMSO, NaCN, 140°, 20 min	 (75) +  (10)	65

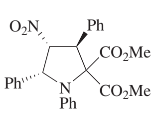
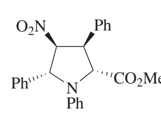
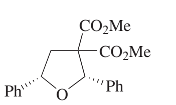
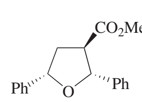
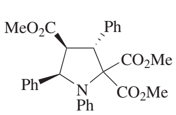
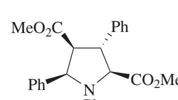
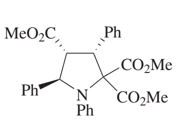
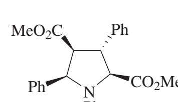
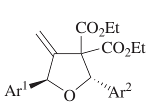
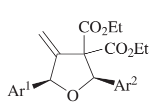
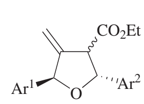
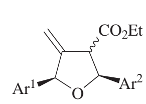
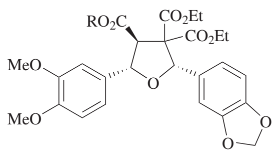
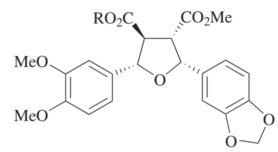
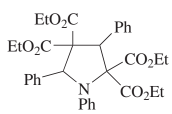
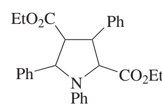
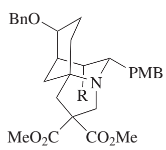
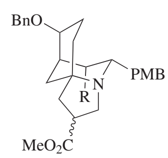
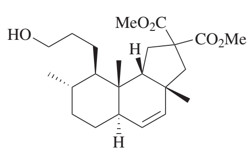
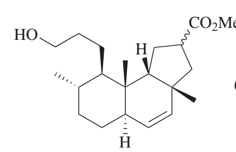
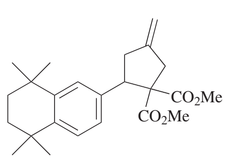
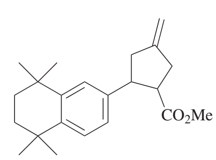
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	PhMe, piperidine, reflux, 48 h	 (79)	953
	DMSO, H_2O, NaCN, 110°, 20 h	 (75) 6.5:1 dr	954, 39
C_{19} 	PhMe, piperidine, reflux, 48 h	 **I** (72)	302
	PhMe, piperidine, reflux, 48 h	 **I** (80)	302
 +  68:32; Ar^1 = 3,4,5-$(MeO)_3C_6H_2$; Ar^2 = 3,5-$(MeO)_2$-4-$BnOC_6H_2$	DMSO, KCN, 150°	 **I** +  **II** ; **I** + **II** (26)	955

TABLE 4C. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

	Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}		See table.		40

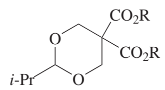
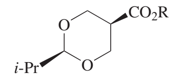
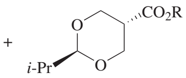
R	Cond.		dr
H	DMSO, H_2O, KOAc, 110°, 16 h	(72)	>20:1
Bn	"variety"	(—)	"low"

	Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}		DMSO, KCN, 140°, 4 h	 (10)	956
	 R = OBn	DMSO, NaCN, Mw, 130°, 40 min	 (61) 1:1 dr	957
C_{21}		DMF, NaCN, 120°, 6 h	 (81)	157
C_{22}		DMF, NaI, $NaHCO_3$	 (70)	958

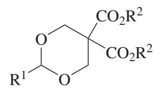
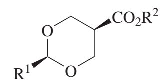
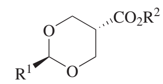
[a] Sixteen percent of the starting material was recovered.

[b] A considerable amount of the acid was also formed. It was converted into the ester with $TMSCH_2N_2$ in benzene/methanol. The yield shown includes that of the re-esterified product.

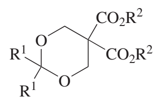
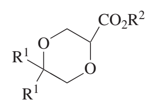
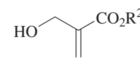
TABLE 4D. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC GEMINAL DIESTERS

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	DMSO, H_2O, LiCl, pyridine, 135°, 3–4 h	 I +  II	43

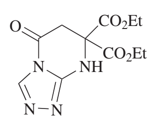
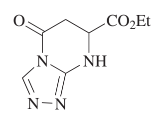
R	I + II	I/II
Me	(—)	86:14
Et	(—)	86:14

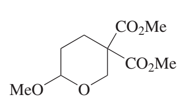
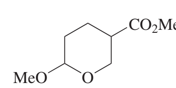
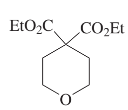
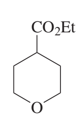
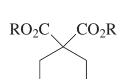
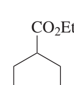
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, additive	 I +  II	

R^1	R^2	Additive	Temp (º)	Time (h)	I	II	Refs.
i-Pr	Et	NaCl	reflux	7	(20)	(57)	44, 43
t-Bu	Me	LiCl	140–145	4	(71)	(9)[a]	45

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl	 I +  II	

R^1	R^2	Temp	Time (h)	I	II	Refs.
Me	Me	reflux	—	(76)	(0)	959, 960
Me	Me	reflux	6	(65)	(20)	961
Me	Et	180°	24	(74)	(0)	962, 963, 964, 965
Et	Et	reflux	19	(79)	(0)	966

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	DMSO, H_2O, NaCl, 190°, 25 min	 (21)	967

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 150°, 10 h	 (81) *cis*/*trans* = 56:44	46, 968
	DMF, LiI, NaCN, 130°, 7 h; then 140°, 25 h	 (92)	969
C_8 	PhH, EtOH, KOH, 18-c-6, rt, time 1; reflux, time 2		330

R	Time 1 (h)	Time 2 (h)	
Me	4	20	(87)
Et	3	22	(70)

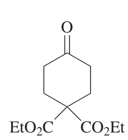
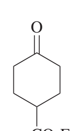
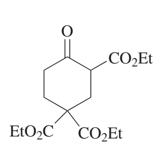
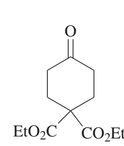
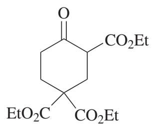
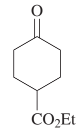
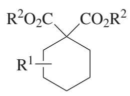
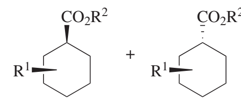
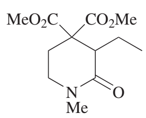
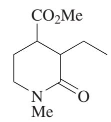
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, pyridine, H_2O, LiCN, 150–160°, 14 h	 (70)	83
C_9 	DMSO, H_2O, NaCl, 150–160°, 2 h	 (83)	83

TABLE 4D. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, H_2O, pyridine, LiCl, 165°, 13 h	 (72)	83
C_{9-12} 	Solvent, H_2O, LiCl, additive	 I + II	
C_9 	DMF, NaCN, reflux, 2 h	 (70)	23

R^1	R^2	Solvent	Additive	Temp (º)	Time (h)	**I + II**	**I/II**	Refs.
2-Me	Et	DMSO	—	187	4	(72)	60:40	42
3-Me	Et	DMSO	—	192	5.5	(79)	48:52	42
4-Me	Et	DMSO	—	196	5.5	(76)	50:50	42
4-*t*-Bu	Me	DMSO	—	194	4	(62)	49:51	42
4-*t*-Bu	Et	DMSO	—	200	5	(69)	49:51	42
4-*t*-Bu	Et	Ph_2O	pyridine	135	—	(—)	53:47	43

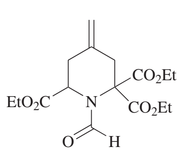
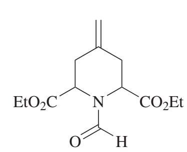
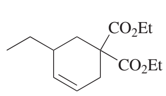
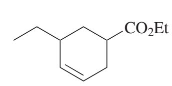
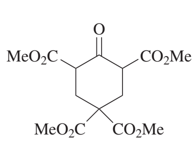
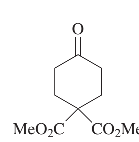
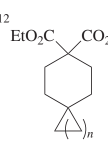
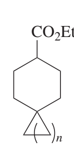
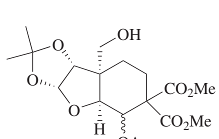
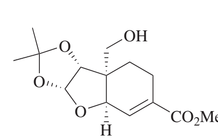
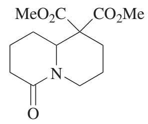
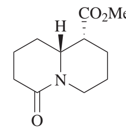
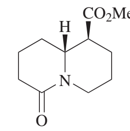
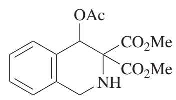
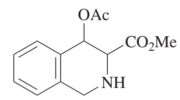
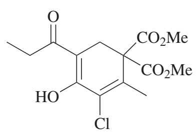
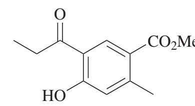
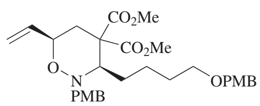
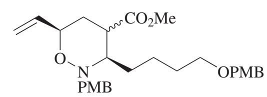
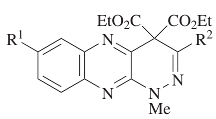
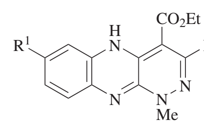
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 165°, 3 h	 (70)	971
C_{10} 	DMSO, H_2O, KCN, reflux, 6 h	 (76) *cis*/*trans* = 1:1	972
	H_2O, 200°, 30 min	 (100)	973
C_{10-12}  n = 1–3	DMSO, H_2O, LiCl, 185°, 10 h	 (48–59)[b]	974
C_{11} 	DMSO, H_2O, NaCl, 110–160°, 3 h; then 160°, 30 min	 (47)	247

TABLE 4D. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	HMPA, LiCl, 80°, 24 h	 (49) +  (19)	975
	MeCN, piperidine, reflux, 48 h	 (80)	976
C_{12} 	DMSO, H_2O, LiCl, 150°, 0.5 h	 (93)	231
 *cis*/*trans* = 12:1	DMSO, H_2O, LiCl, 160°	 (85) 1:1 mixture of diastereomers	977
	EtOH, H_2NNH_2•H_2O, reflux, 1 h	 R^1 R^2 H Cl (79) H Br (78) Cl Cl (95) Cl Br (92)	978

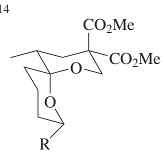
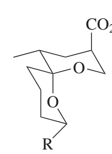
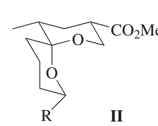
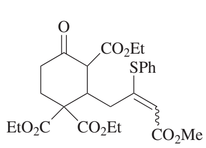
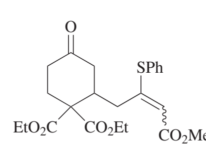
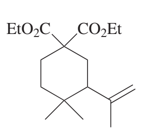
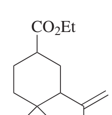
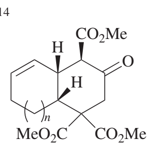
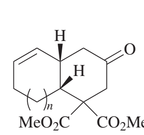
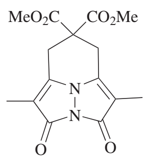
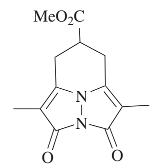
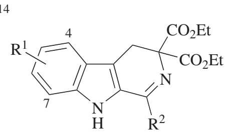
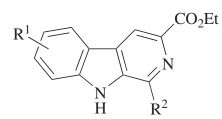
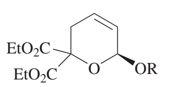
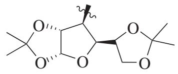
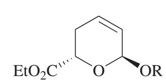
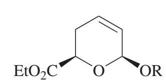
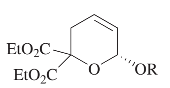
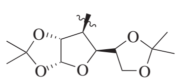
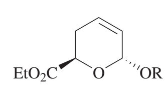
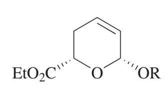
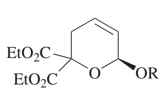
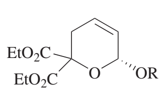
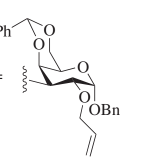
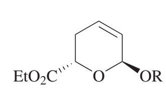
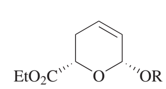
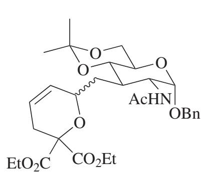
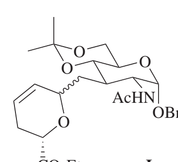
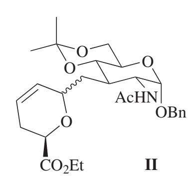
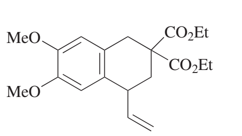
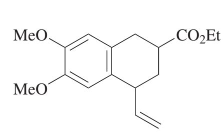
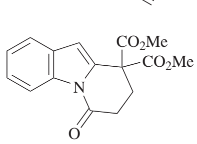
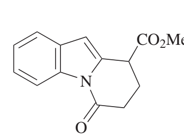
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{12–14}$ 	DMSO, H_2O, LiCl, 160°, 100 min	 **I** +  **II** R **I + II** **I/II** H (86) 83:17 Et (79) 80:20	47
C_{13} 	DMF, LiI, 125–130°, 2.5 h	 (68)	979
	DMSO, H_2O, LiCl, reflux, 4–5 h	 (68) *trans*/*cis* = 55:45	980
$C_{13–14}$ 	DMSO, H_2O	 *n* Temp (°) Time (h) 1 150 15 (68) 2 140 2 (80)	84

TABLE 4D. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

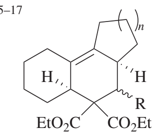
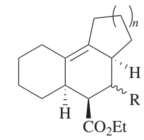
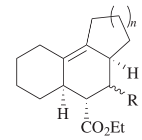
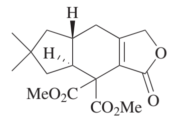
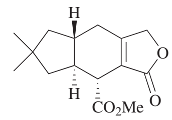
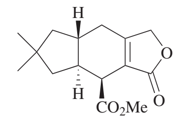
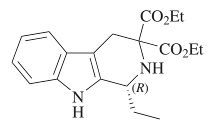
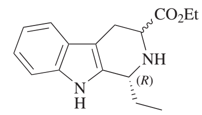
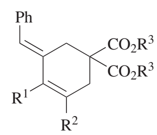
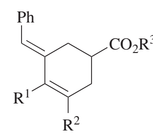
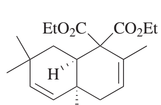
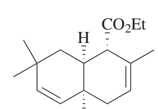
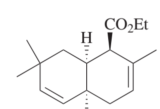
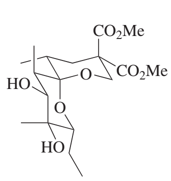
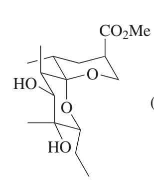
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	DMF, LiI•2H_2O, reflux, 15 h	 (33)	981
C_{13-14} 	DMSO, H_2O, LiCl, 170°, 7–9 h		982
C_{13}  R = 	HMPA, H_2O, NaCl, 180–190°, 2.5 h	 **I** +  **II**; **I** + **II** (82), **I**/**II** = 64:18	970
 R = 	HMPA, H_2O, NaCl, 180–190°, 2.5 h	 **I** +  **II**; **I** + **II** (85), **I**/**II** = 71:16	970
 +  R = 	1. HMPA, H_2O, NaCl, 195°, 2 h 2. BF_3•Et_2O	 **I** +  **II**; **I** + **II** (87), **I**/**II** = 60:20	970
C_{14} 	DMSO, H_2O, LiCl, 170°, 3 h	 **I** +  **II**; **I** + **II** (98)	34
	DMSO, H_2O, LiCl, 150°	 (80) 3:2 dr	983
	DMF, H_2O, LiCl, Mw, 150°, 10 min	 (65)	326

Ref. 982 products:

R^1	R^2	
5-CHONH	H	(30)
5-AcNH	H	(35)
6-AcNH	H	(42)
6-AcNH	Me	(30)
7-CHONH	H	(30)
7-AcNH	H	(34)
7-AcNH	Me	(31)

Ref. 34 products:

Config.	**I/II**
α	1:20
β	20:1

Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-17} 	DMSO, NaCN, 160°, 4 h	 **I** +  **II**	
C_{15} 	DMF, NaCN, reflux, 4 h	 **I** +  **II** **I + II** (70), **I/II** = 2:1	63
	DMSO, H_2O, LiCl, 180°, 4 h	 (—)	986
C_{16-19} 	Reflux		295
C_{16} 	DMSO, NaCN, 160°, 6 h	 **I**[d] +  **II** **I + II** (70), **I/II** = 8:1	59
	DMSO, H_2O, LiCl, 165–170°, 90 min	 (83) "predominant isomer"	987

n	R	**I + II**	**I/II**	Refs.
1	H	(95)	55:45	984
2	H	(70)	80:20	985
2	Me	(—)	98:2	985

R^1	R^2	R^3	Solvent	Additive	Time (h)	
Me	H	Et	*p*-xylene	DMAP	96	(44)
Me	MeO_2C	Me	MeCN	DBU	20	(73)[c]
Me	MeO_2C	Et	MeCN	DBU	20	(73)[c]
Me	EtO_2C	Et	MeCN	DBU	20	(82)[c]
Me	NC	Et	MeCN	DBU	16	(47)[c]
Me	MeCO	Me	MeCN	DBU	1	(87)[c]
Me	MeCO	Et	MeCN	DBU	1	(84)[c]
Me	EtCO	Et	MeCN	DBU	3	(65)[c]
Et	MeO_2C	Et	MeCN	DBU	8	(50)[c]
Et	MeCO	Et	MeCN	DBU	1	(87)[c]

TABLE 4D. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

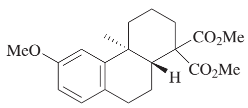
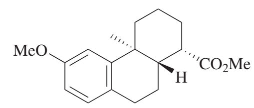
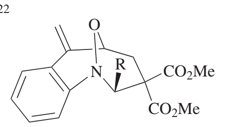
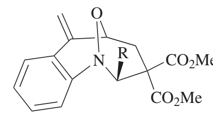
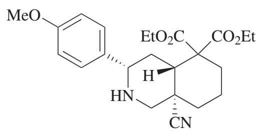
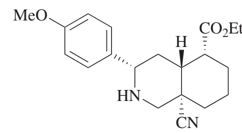
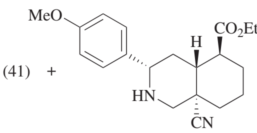
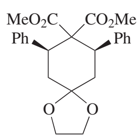
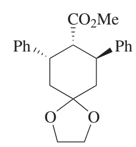
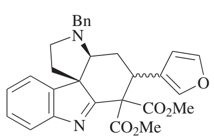
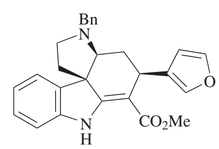
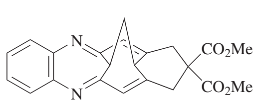
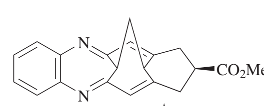
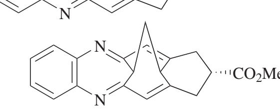
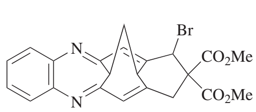
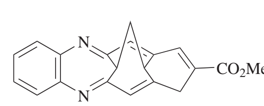
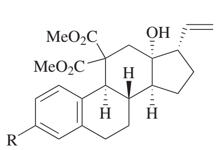
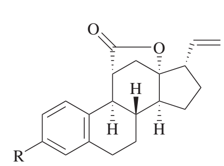
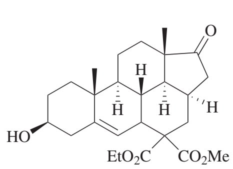
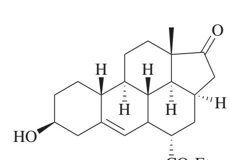
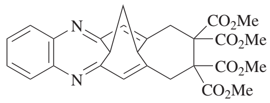
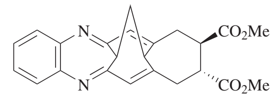
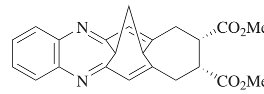
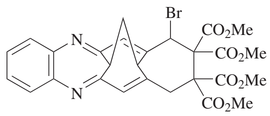
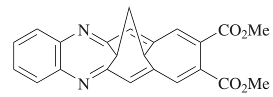
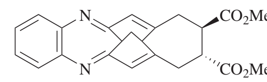
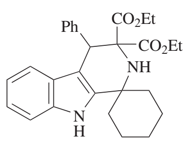
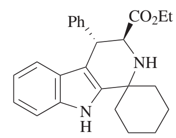
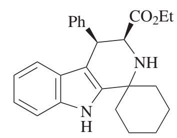
Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	DMSO, H_2O, NaCl, 180°	 (—)	988
C_{18-22} 	DMSO, H_2O, LiCl, 160°, 1.5 h	 R / dr: 2-furyl (58) 5:2; Ph (87) 3:1; 3,4-(OCH_2O)C_6H_3 (80) 5:2; 3,4,5-$(MeO)_3C_6H_2$ (78) 4:1; *N*-tosyl-3-indolyl (56) 5:2	66
C_{18} 	DMF, H_2O, LiCl, reflux, 48 h	 (41) +  (29)	64
C_{20} 	DMSO, H_2O, NaCl, 184°, 8 h	 (93) racemic	70
	DMA, LiCl, Et_3NHCl, 130°, 45 min	 (48)	646
	DMF, H_2O, LiCl, 110°, 10 h	 (24) +  (27)	989
	DMF, H_2O, LiCl, 110°, 3.5 h	 (68)	989
C_{21} 	DMSO, KCN, 90°	 R: H (—); MeO (—)	169
C_{23} 	DMSO, LiCl, 150°	 (76)	160

TABLE 4D. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

	Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}		DMF, H_2O, LiCl, 110°, 24 h	 **I** +  **II** **I** + **II** (83)[e], **I/II** = —	989
		DMF, H_2O, LiCl, 110°, 18 h	 (20) +  (10)	989
C_{24}		DMSO, H_2O, LiCl, 180°, 7 h	 **I** +  **II** **I** + **II** (98), **I/II** = 3:2	990

[a] Treatment of the isomer mixture with NaOMe in MeOH gave a 16.5:83.5 mixture of *cis* and *trans* isomers.

[b] The yield is for the three steps from the diols: tosylate formation, ring formation with diethyl sodiomalonate, and dealkoxycarbonylation.

[c] The yield and reaction time include those of the preparation of the substrate.

[d] The authors state that the α-isomer is the major product but then refer by number, presumably in error, to a structure that is the β-isomer.

[e] Isomer **I** was obtained in 48% yield by fractional crystallization.

TABLE 4E. DEALKOXYCARBONYLATIONS OF SEVEN- AND HIGHER-MEMBERED CYCLIC GEMINAL DIESTERS

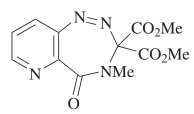
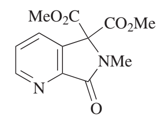
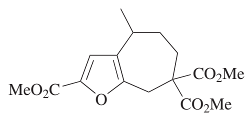
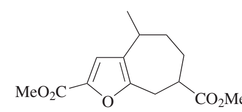
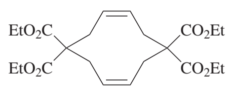
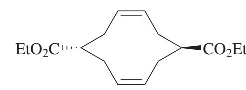
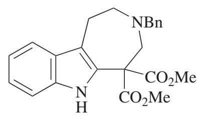
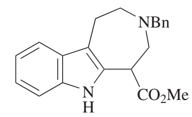
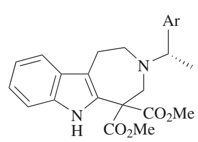
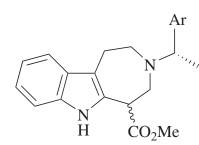
	Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		DMSO, NaCl, 110°, 10 min	 (26)	991
C_{13}		DMF, H_2O, NaCl, 140–160°, 4 h	 (60)	992
C_{14}		Krapcho	 (—)	161
		DMF, H_2O, LiCl, 160–165°, 1 h	 (83)	993
		DMA, Et_3NHCl, LiCl, 1 h	 Ar / Temp (°): Ph, 120 (80); 1-naphthyl, 130 (68)	994

TABLE 4E. DEALKOXYCARBONYLATIONS OF SEVEN- AND HIGHER-MEMBERED CYCLIC GEMINAL DIESTERS (*Continued*)

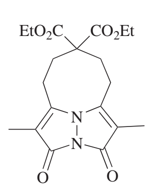
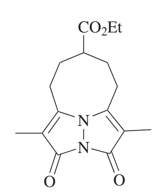
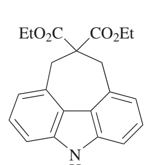
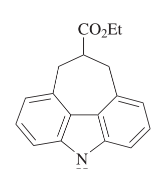
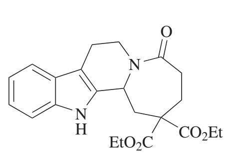
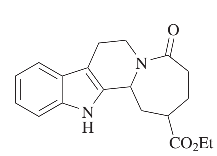
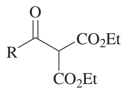
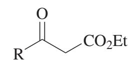
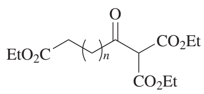
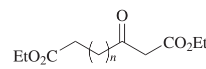
	Cyclic Geminal Diester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		DMF, LiBr, reflux, overnight	 (72)	995
C_{17}		DMSO, NaCN, 160°, 8 h	 (50)	996
C_{18}		DMSO, H_2O, LiCl, 170–180°, 5 h	 (96) mixture of diastereomers	997

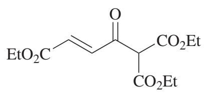
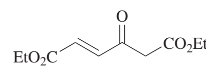
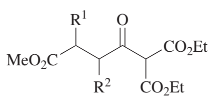
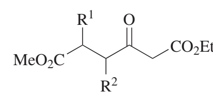
TABLE 5. DEALKOXYCARBONYLATIONS OF α-ACYL MALONATES

α-Acyl Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-13} 	See table.		

R	Solvent	Additive(s)	Temp	Time (h)		Refs.
Et	H_2O	—	slow distillation	—	(75)	998–1001
$Cl(CH_2)_3$	H_2O	brine	reflux	2	(53)	1002, 1003
n-C_9H_{19}	n-$C_9H_{19}CO_2H$	MgO, $Cu(OAc)_2$	140–160°	7	(—)	1004

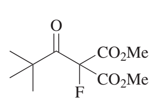
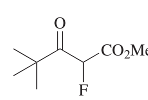
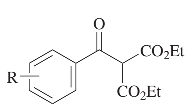
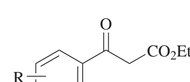
α-Acyl Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-9} 	H_2O		

n	Temp (º)	Time (h)		Refs.
1	distillation	—	(65)	1005
1[a]	150	0.5	(65–70)	1006
2[a]	150	0.5	(65–70)	1006
3[a]	150	0.5	(65–70)	1006

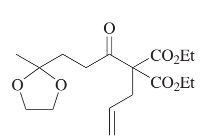
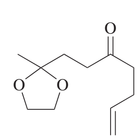
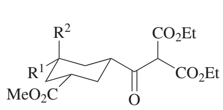
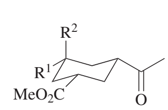
α-Acyl Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	H_2O (2 eq), 120°, 20 min	 (62)[b]	1007
C_8 	H_2O, reflux		

R^1	R^2	Time (h)		Refs.
H	Me	3	(63)	1008
H	$MeOCH_2$	1	(53)	
$MeOCH_2$	H	1.5	(57)	

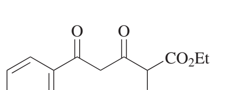
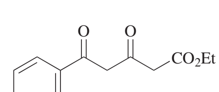
TABLE 5. DEALKOXYCARBONYLATIONS OF α-ACYL MALONATES (*Continued*)

α-Acyl Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	DMSO, H_2O, NaCl, 150–160°, 15 min	 (32)	229
C_{10} 	See table.		

R	Cond.		Refs.
H	H_2O, distillation	(—)	1009
3-BnO, 4-MeO	EtOH (95%), NaOAc, reflux, 7 h	(91)	1010

α-Acyl Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl	 (—)	1011
	DMSO, H_2O, NaCl, 160–170°, 6 h		1012

R^1	R^2	
H	H	(80)
MeO	H	(69)
—$O(CH_2)_2O$—		(61)

α-Acyl Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	H_2O, autoclave, 3 atm, 130°	 (—)	1013

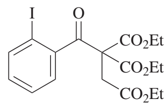
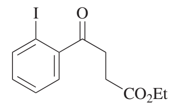
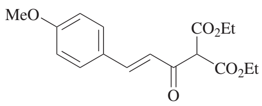
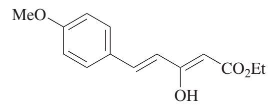
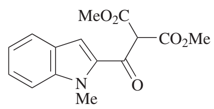
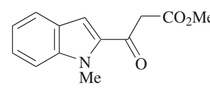
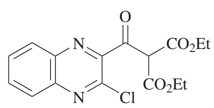
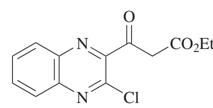
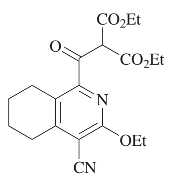
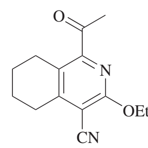
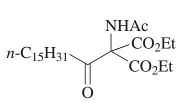
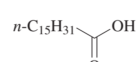
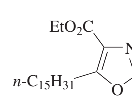
	DMSO, H_2O, NaCl, 120°, 2–4 h	 (51)	162
	DMSO, H_2O, NaCl, 130–140°, 2 h	 (77)	163
	THF, H_2O, basic Al_2O_3, reflux, 4 h	 (87)	320, 1014
	H_2O, NaCl, 90–95°, 1.75 h	 (66)	1015
C_{14} 	DMSO, H_2O, NaCl, 165–170°, 4 h	 (63)	1016

TABLE 5. DEALKOXYCARBONYLATIONS OF α-ACYL MALONATES (*Continued*)

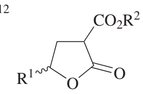
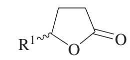
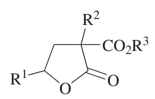
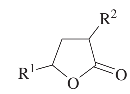
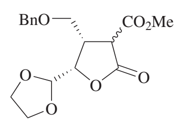
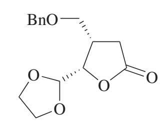
α-Acyl Malonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19} 	DMSO, H_2O, LiX, 120°, 2 h	 X: Cl (—); Br (—)	1017
	See table.		1017

Solvent	Additive	Temp (º)	Time (h)	
DMSO	H_2O	189	2	(62)
DMF	H_2O	153	4	(70)
NMP	H_2O	202	0.25	(83)

[a] The ratio of substrate to water was 1:1 and the reaction was carried out in a closed vessel.

[b] At 150° under otherwise identical conditions, the cleavage product, (*E*)-ethyl 4-oxopentenoate, was formed in 64% yield.

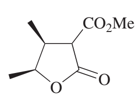
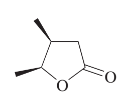
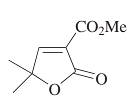
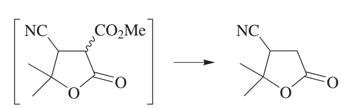
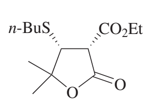
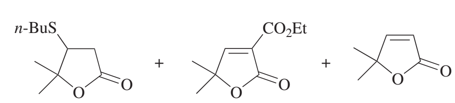
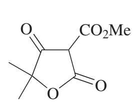
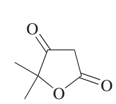
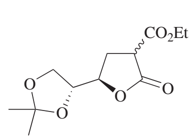
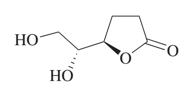
TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-12} 	See table.		
C_6 	DMSO, H_2O, NaCl		
C_7 	DMSO, H_2O, LiCl, 100°, 25 h	 (84)	1025

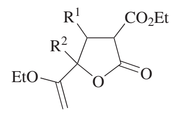
R^1	C-5 Config.	R^2	Solvent	Additive(s)	Temp	Time (h)		Refs.
Me	(*S*)	Me	DMSO	H_2O, LiCl	reflux	3.5	(—)	1018
Me	(*S*)	Et	DMF	H_2O	reflux	10	(—)	1019
$BnOCH_2$	(*R*)	Et	DMA	H_2O, $MgCl_2$	reflux	2	(90)	1021
i-Pr	(*R*)	Me	DMSO	H_2O, NaCl	130°	6	(47)[a]	1020
$MeCH(OBn)CH_2$	(*R*,*S*)	Et	DMF	$MgCl_2•2H_2O$	reflux	3	(70)[a]	1022
$MeCH(OTBDPS)CH_2$	(*R*,*S*)	Et	DMF	$MgCl_2•2H_2O$	reflux	3	(83)[a]	1022
PhCH(OAc)	(*R*,*S*)	Et	DMF	LiI	140°	8	(75)[b]	1023

R^1	R^2	R^3	Temp (°)	Time (h)		Refs.
$TBDPSCH_2$	H	Me	160–170	4	(85)	159, 1024
N_3CH_2	F	Et	reflux	2.5	(73)	743

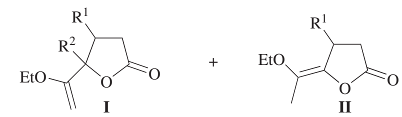
TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	DMSO, H_2O, LiCl, reflux, 3.5 h	 (60)	1018
	1. DMSO, NaCN, rt, 40 h 2. DMSO, H_2O, 140°, 40 h	 (98)	250
	DMSO, H_2O, 140°, 40 h	 (63) + (14) + (18)	250
	$MeNO_2$, H_2O, reflux, 35 min	 (—)	1026
	DMA, $MgCl_2•2H_2O$, reflux, 3 h	 (80)	1027, 1028

C_{7-9}



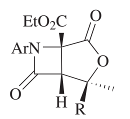
DMSO, H_2O, NaCl, 160°, 3 h



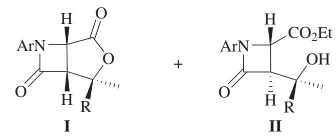
R^1	R^2	**I**	**II**
H	H	(68)	(11)
H	Me	(92)	(0)
Me	Me	(80)	(0)

Refs. 1029

C_{7-8}



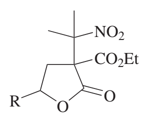
Solvent, H_2O, NaCl, reflux



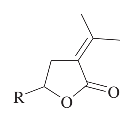
Ar	R	Solvent	Time (h)	**I**	**II**
4-$MeOC_6H_4$	H	DMF	8	(0)	(70)
4-$MeOC_6H_4$	Me	DMF	12	(40)	(29)
4-MeC_6H_4	Me	DMSO	4	(79)	(0)

Refs. 184

C_{8-9}



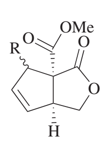
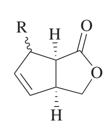
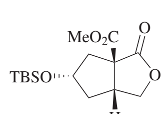
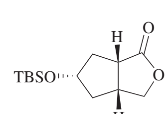
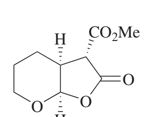
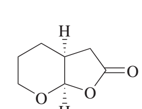
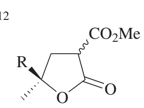
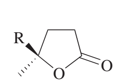
HMPA, NaBr, 130–140°, 4 h



R	
H	(50)[a]
Me	(55)[a]

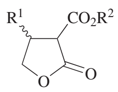
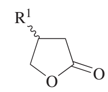
Refs. 233

TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	DMF, LiI, reflux		1030
C_8 	DMSO, H_2O, LiCl, 140°, 12 h	 (99)	49
	DMF, H_2O, reflux	 (64)	1031
C_{9-12} 	DMF, H_2O, reflux, 12 h		1032

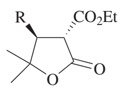
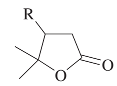
R	Config. (Substrate and Product)	Time (h)	
H	—	2.5	(60)
Me	α/β = 83:17	2	(91)

R	
i-Pr	(17)[c]
Ph	(43)[c]

	DMSO, H_2O, additive		

R^1	R^2	Config.	Additive	Temp (°)	Time (h)		er	Refs.
n-Bu	Me	(*S*)	NaCl	130–150	6	(83)	—	91, 1033
i-Bu	Et	(*S*)	LiCl	140	18	(79)	99.5:0.5	92
3-$MeOC_6H_4CH_2$	*t*-Bu	(*R*)	LiCl	140	17	(65)	96.0:4.0	93

C_{9-13}

	See table.		250

R	Solvent	Additive(s)	Temp (°)	Time (h)	
Et	DMSO	H_2O	140	24	(87)
n-Pr	DMSO	H_2O	140	24	(90)
n-Pr	DMSO	H_2O, NaCl	170	—	(0)
n-Pr	HMPA	H_2O, KCN	—	—	(60)
Ph	DMSO	H_2O	140	24	(73)

C_9

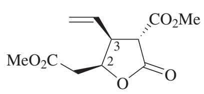
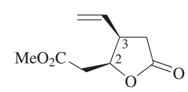
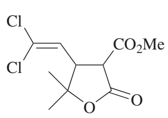
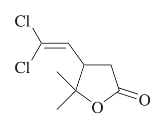
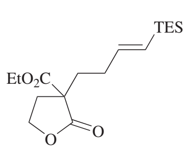
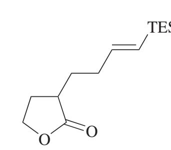
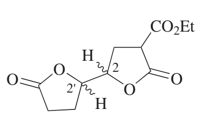
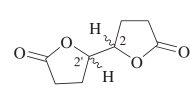
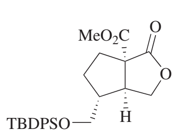
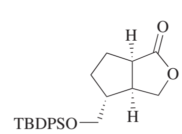
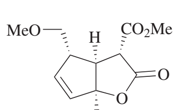
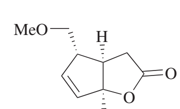
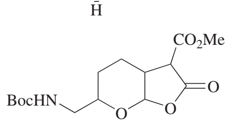
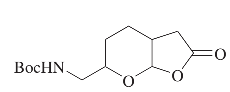
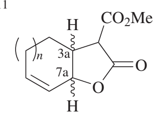
	DMF, H_2O, reflux, 2 h	 Config.: (2*SR*,3*RS*) (82); (2*S*,3*R*) (85)	1034, 1035
	DMF, H_2O, 120–140°, 4–12 h	 (95)	1036, 1037

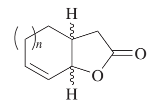
TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	DMSO, H_2O, LiCl, reflux, 3 h	 (77)	1038
	DMA, H_2O, $MgCl_2$, reflux, 7 h	 Config.: (2*S*,2′*S*) (78); (2*R*,2′*R*) (73); (2*R*,2′*S*) (75)	1039
	DMSO, H_2O, LiCl, 160°, 2 h	 (90)	1040
	DMSO, H_2O, LiCl, 110°	 (83)	1041
	DMF, H_2O, LiCl, 150°, 12 h	 (57)	1042

C9–11



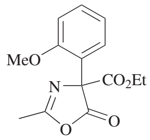
DMSO or DMF, H_2O, NaCl, 150°, 3–5 h



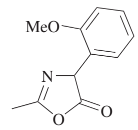
n	C-3a, C-7a Config.	
1	*cis*	(70–80)
3	*trans*	(70–80)

1043

C9



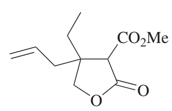
H_2O/EtOH (4:1), sonication, <40°, 11 h



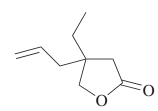
(60)

1044

C10

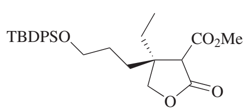


DMF, H_2O, NaCl, 160°, 12 h

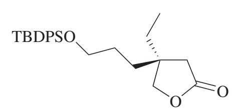


(72)

1045

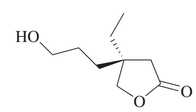


DMSO, H_2O, NaCl, 12 h



I

\+



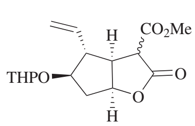
II

Temp (°)	I	II	Refs.
110	(84)	(0)	177
160	(48)	(42)	1046

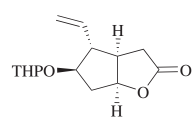
TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

C10



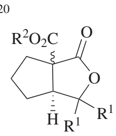
Pyridine, LiI, reflux, 3 h



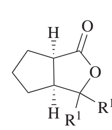
(37)

1047

C10–20

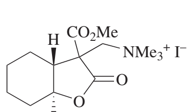


See table.

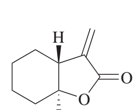


R^1	R^2	Config.	Solvent	Additives	Temp (°)	Time (h)		Refs.
Me	Me	*cis*	dioxane	H_2O, Al_2O_3	—	—	(—)	1048
Me	Me	*trans*	dioxane	H_2O, Al_2O_3	—	—	(—)	1048
Me	Et	*cis*	DMSO	H_2O, LiCl	195	3	(40)	1049
Ph	Et	*cis*	DMSO	H_2O, LiCl	195	3	(64)	1049

C10

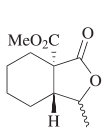


DMF, 80°, overnight

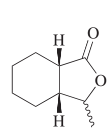


(100)

1050



HMPA, NaCN, 100°, 12 h



(69)

50

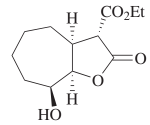
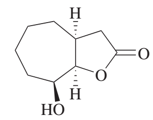
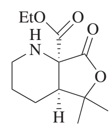
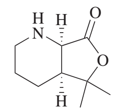
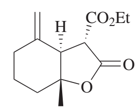
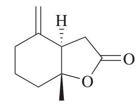
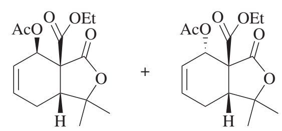
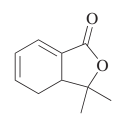
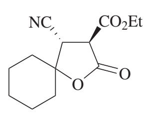
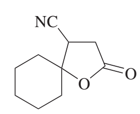
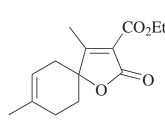
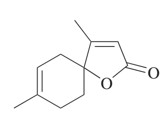
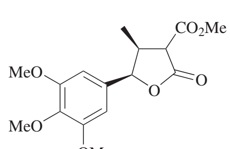
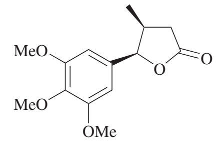
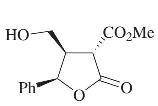
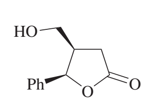
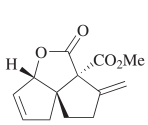
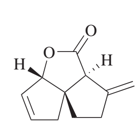
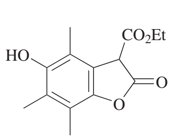
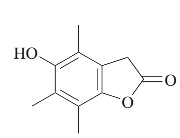
α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 140–180°, 40 min; then 180°, 50 min	 (95)	1051
	DMF or DMSO, LiCl or NaCl or NaCN, rt to 180°	 (30)	1052
C_{11}			
	DMF, LiBr, reflux, 8 h	 (90)	1053
 4:1	2,4,6-Collidine, LiI•$2H_2O$, reflux, 1 h	 (50)	1054
	DMSO, H_2O, NaCl, reflux, 5 h	 (60)	1055

TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	DMSO, H_2O, NaCl, 160°, 2 h	 (90)	1056
	DMSO, H_2O, NaCl, 140°	 (—)	1057
	DMSO, NaCl, 110°, 14 h	 (57)	1058
	DMSO, H_2O, LiCl, 150°	 (77)	1059
	DMSO, H_2O, 110–120°, 1 h	 (99)	1060

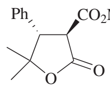
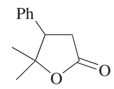
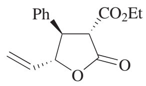
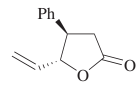
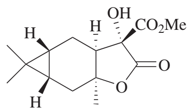
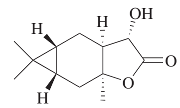
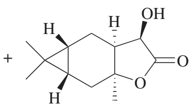
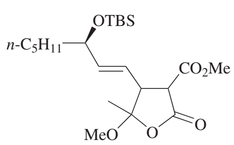
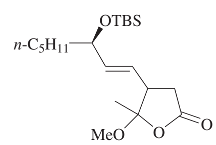
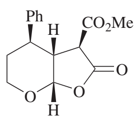
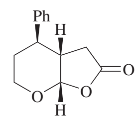
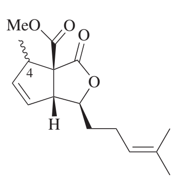
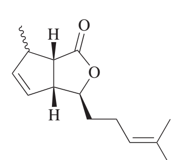
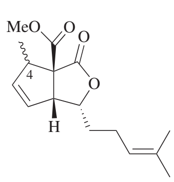
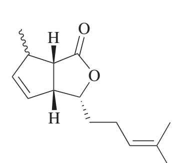
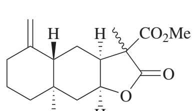
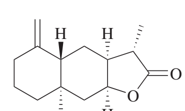
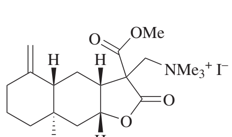
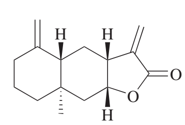
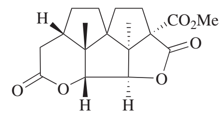
C_{13}			
	DMSO, H_2O, NaCl, 170–210°, 3 h	 (87)	1061
	DMSO, LiCl, 140°	 (89)	1062
	DMF, H_2O, NaCl, 150°, 3 h	 I +  II **I + II** (84), **I/II** = 68:32	1063
C_{14}			
	DMSO, H_2O, NaCl	 (—)	1064
	DMF, H_2O, reflux	 (95)	1031

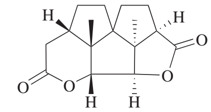
TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	DMF, LiI, reflux, 3 h	 C_4-Config. α (83) β (90)	1065
	DMF, LiI, reflux, 3 h	 C-4 Config. α (40) β (71)	1065
C_{16}			
	HMPA, NaCN, 80°, 1 h	 (91)	1066
	DMF (anhyd), 80°, 16 h	 (100)	1067

C$_{17}$

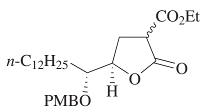


DMSO, H_2O, NaCl, 180°

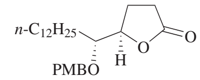


(—) 1068

C$_{18}$

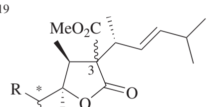


DMA, $MgCl_2$•$6H_2O$, reflux, 3 h

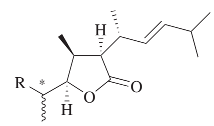


(—) 1028, 1027

C$_{18–19}$



DMSO, H_2O, LiCl



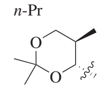
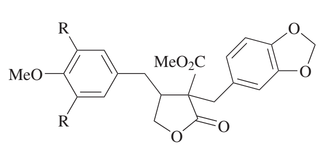
R	C-3 dr	* Config.	Temp (°)	Time (h)		Refs.
n-Pr	—	(*S*)	150	19	(69)[d]	1069
	56:44	(*R*)	190	3	(87)[e]	1070

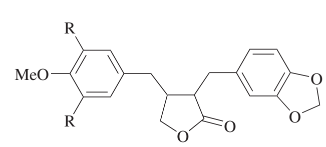
TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

C$_{19}$



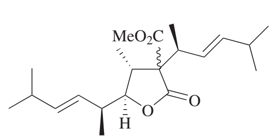
DMF, additive, 130°, 4 h



1071

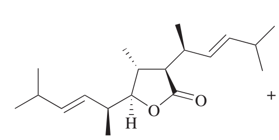
R	Additive	[a]	*trans/cis*
H	LiCl	(87)	85:15
H	NaCl	(92)	85:15
MeO	LiCl	(94)	major isomer *trans*

C$_{20}$



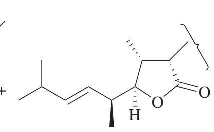
2:1 dr

DMSO, H_2O, LiCl, 200°, 3 h



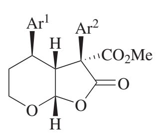
(91)

+

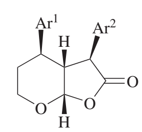


(4)

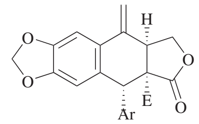
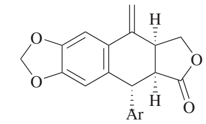
1072, 1073



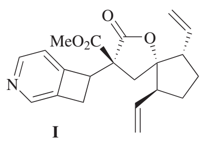
Solvent, additive, reflux



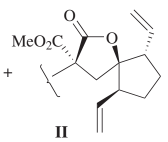
Ar[1]	Ar[2]	Solvent	Additive(s)	Time (h)		dr	Refs.
Ph	4-MeOC$_6$H$_4$	DMSO	H_2O, NaCl	2	(81)	7.5:1	1074
Ph	4-TIPSOC$_6$H$_4$	DMSO	H_2O, NaCl	2	(0)[f]	—	1074
2,4,6-(MeO)$_3$C$_6$H$_2$	4-MeOC$_6$H$_4$	DMF	LiI	5	(67)	—	1075

 $E = CO_2Me$	DMSO, H_2O, NaCl, 155°		1076

Ar	
2,3,4-$(MeO)_3C_6H_2$	(90)
2,4,6-$(MeO)_3C_6H_2$	(70)

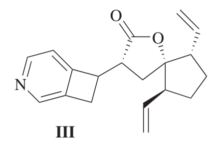

I

+

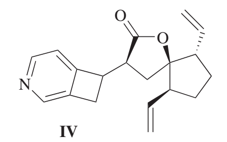

II

I/II = 7:3

DMSO, NaCN, 90°, 24 h


III

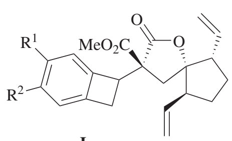
+


IV

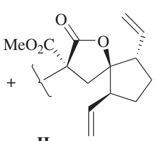
III + IV (91), **III/IV** = —

1077, 1078

C_{21}

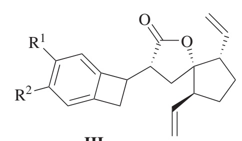

I

+

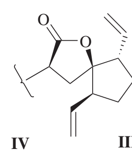

II

I/II = —

DMSO, NaCN, 90°


III

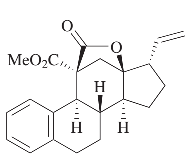
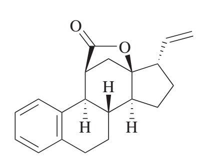
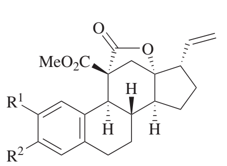
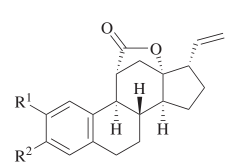
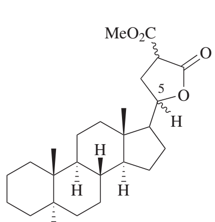
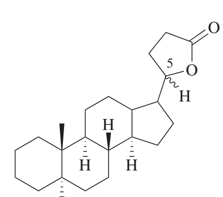
+


IV

III/IV = —

R^1	R^2	**III + IV**	Refs.
H	H	(90)	169
H	MeO	(83)	169
H	*t*-BuO	(62)	1079
F	H	(69)	1080
MeO	MeO	(88)	169
t-BuO	H	(78)	1080

TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	DMSO, NaCN, 100°, 19 h	 (—)	1081
	DMSO, NaCN, 80°		169
C_{24}			
	DMSO, H_2O, NaCl, 170°, 6 h		1082

R^1	R^2	
H	H	(71)
H	MeO	(63)
MeO	MeO	(91)

C-5 Config.	
(*R*)	(35)
(*S*)	(18)

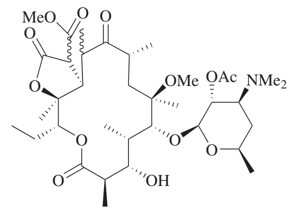
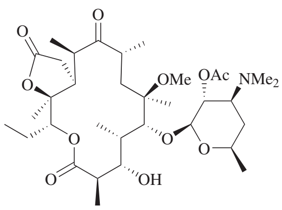
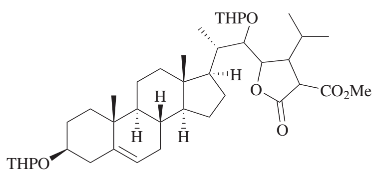
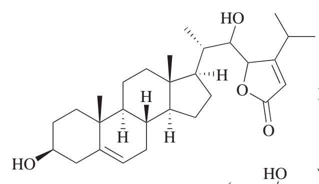
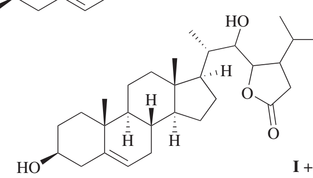
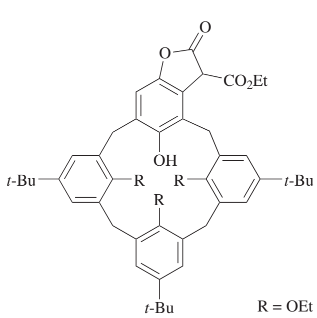
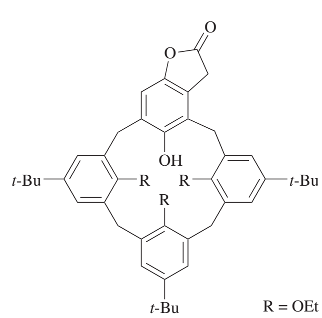
C_{30} 	DMSO, LiCl, reflux, 4 h		(33)	1083
	DMF, LiI, $CaCO_3$, I_2, 150°, 2 h	 **I** +  **II** **I + II** (80), **I/II** = 1:1		1084

TABLE 6A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{43}  R = OEt	DMSO, 110–115°, 2 h	 R = OEt	(68)	1085

[a] The yield includes that of the preparation of the substrate.

[b] The substrate was a mixture of four diastereomers which led to a mixture of two isomers.

[c] The yield is for three steps.

[d] In addition, a mixed fraction containing a 2:1 ratio of the 3-α and 3-β isomers was isolated in 15% yield.

[e] The number is the yield obtained of a 98:2 mixture of the 3-α and 3-β isomers by treating the initial product mixture with KO*t*-Bu in *t*-BuOH/Et_2O at room temperature.

[f] The reference reported decomposition of the product.

TABLE 6B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED α-ALKOXYCARBONYL LACTONES (*Continued*)

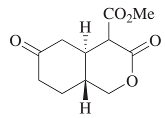
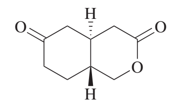
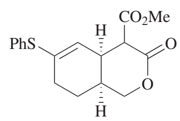
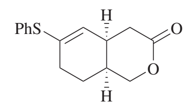
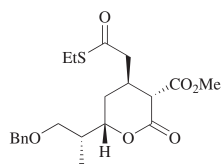
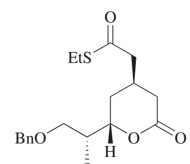
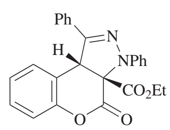
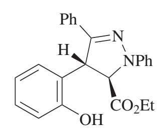
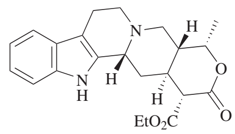
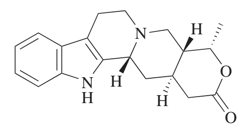
α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	DMSO, H_2O, LiCl, 100°, 19 h	 (30)	542
	DMSO, H_2O, LiCl, 120°, 4.5 h	 (66)	542
C_{11}			
	DMSO, H_2O, NaCl, 175°	 (86)	1090
C_{17}			
	DMSO, H_2O, NaCl, 150°, 2 h	 (60)	180
C_{20}			
	DMSO, NaCN, 80°, 48 h	 (—)	1091

TABLE 6C. DEALKOXYCARBONYLATIONS OF SEVEN- AND HIGHER-MEMBERED α-ALKOXYCARBONYL LACTONES

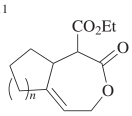
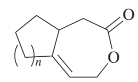
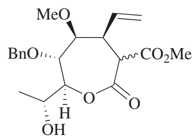
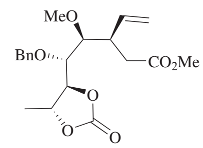
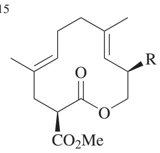
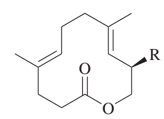
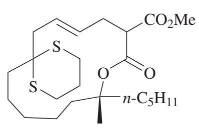
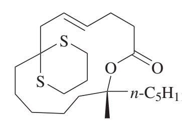
α-Alkoxycarbonyl Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11} 	DMSO, H_2O, NaCl	 *n*: 1 (—); 2 (—)	1092
C_{11} 	DMSO, H_2O, LiCl, heat	 (78)	181
C_{14-15} 	Krapcho	 R: H (91); Me (93)	1093
C_{19} 	DMSO, H_2O, LiCl, reflux, 65 min	 (78)	179

TABLE 7. DEALKOXYCARBONYLATIONS OF α-ALKOXYCARBONYL AMIDES

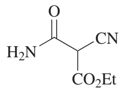
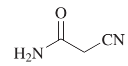
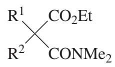
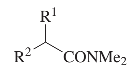
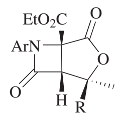
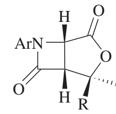
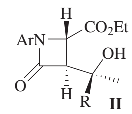
α-Alkoxycarbonyl Amide	Conditions	Product(s) and Yield(s) (%)					Refs.
C_4							
	H_2O, reflux, 5 h	 (49)					1094
C_{9-11}			R^1	R^2	Time (h)		
	2,4-Lutidine, LiI, reflux		H	Bn	15	(92)	285
			Me	(*E*)-MeCH=CHCHMe	2.5	(66)	
			Me	Bn	2.5	(70)	

TABLE 8A. DEALKOXYCARBONYLATIONS OF FOUR-MEMBERED α-ALKOXYCARBONYL LACTAMS

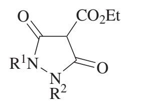
α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	Solvent, H_2O, NaCl, reflux	 I +  II	184

Ar	R	Solvent	Time (h)	I	II
4-$MeOC_6H_4$	H	DMF	8	(0)	(70)
4-$MeOC_6H_4$	Me	DMF	12	(40)	(29)
4-MeC_6H_4	Me	DMSO	4	(79)	(0)

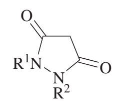
TABLE 8B. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTAMS

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.

C_4

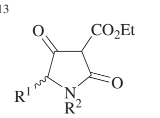


MeCN, H_2O, reflux

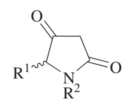


R^1	R^2	Time (h)		Refs.
—$(CH_2)_4$—		6	(60)	1095
Me	Bn	5	(97)	1096
n-Pr	*n*-Pr	3	(41)	1095
Ph	Bn	5	(76)	1096
Bn	Bn	3	(78)	1095
$EtO_2C(CH_2)_6$	*n*-C_8H_{17}	2.5	(59)	1097
$EtO_2C(CH_2)_6$	*n*-$C_5H_{11}CH(OH)(CH_2)_2$	2.5	(—)	1097
$EtO_2C(CH_2)_6$	*c*-$C_6H_{11}CH(OH)(CH_2)_2$	2.5	(—)	1097

$C_{5–13}$

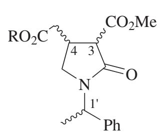


MeCN, H_2O, reflux

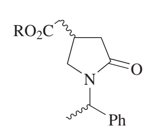


R^1	R^2	Config.	Time (h)		Refs.
H	Bn	—	2	(95)	1098
Me	H	(*S*)	6	(40)	1099
Me	3,4-$(MeO)_2C_6H_3CH_2$	(*R*)	3	(100)	1100
CH_2=$CH(CH_2)_6$	3,4-$(MeO)_2C_6H_3CH_2$	(*R,S*)	—	(84)[a]	1101

C_6

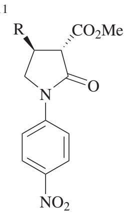


DMF, H_2O, NaCl, 3 h

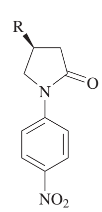


	Config.					
R	C-1'	C-3	C-4	Temp (°)		Refs.
Me	(*S*)	(*R*)	(*R*)	reflux	(77)	1106
Me	(*S*)	(*S*)	(*S*)	reflux	(75)	1106
Et	(*R*)	(*R*)	(*R*)	80	(76)	1107
Et	(*R*)	(*S*)	(*S*)	80	(78)	1107

$C_{6–11}$

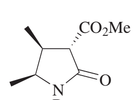


DMSO, H_2O, NaCl, 160°, 2 h

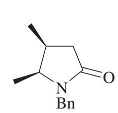


R		Refs.
Me	(—)	
Et	(—)	
4-ClC_6H_4	(96)	1102
4-$O_2NC_6H_4$	(—)	
4-$MeOC_6H_4$	(—)	

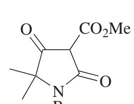
C_7



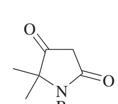
DMF, H_2O, NaCl, reflux, 8 h



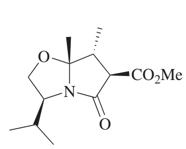
(81) 1103



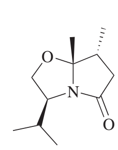
$MeNO_2$, H_2O, reflux, 35 min



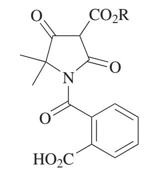
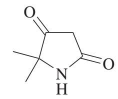
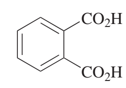
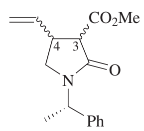
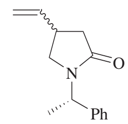
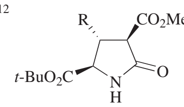
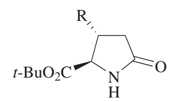
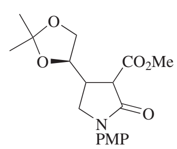
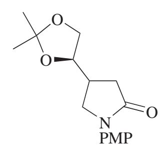
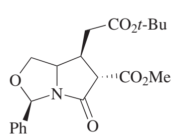
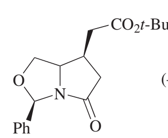
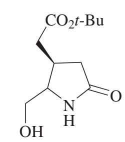
(—) 1026

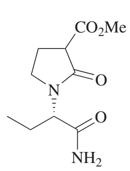
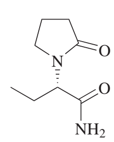
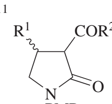
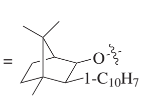
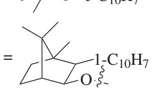
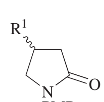
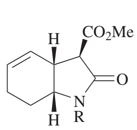
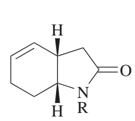
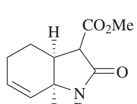
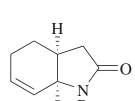


PhMe, DMAP, pH 7, reflux, 5 d



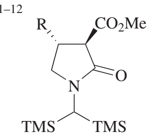
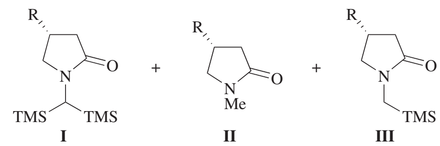
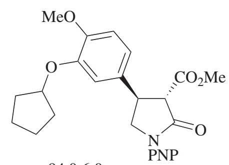
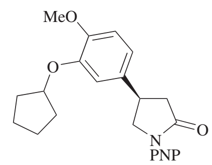
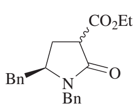
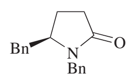
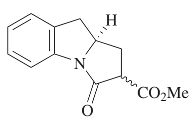
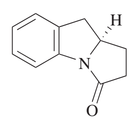
(51)[b] 301

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	H_2O, 100°, 5 h	 R: Me (—); Et (56) + 	1104
	DMF, H_2O, NaCl, reflux, 3 h	 Config. C-3, C-4: (*R*) (*R*) (79); (*S*) (*S*) (77)	1106
$C_{7–12}$ 	DMEU, H_2O, LiCl, 4 h	 R / dr / Temp (°): Me, 86:14, 140 (80); Ph, 100:0, 130 (88)	1108
C_7 	DMSO, H_2O, NaCl, 110°, 28 h	 (92) mixture of diastereomers	1109
C_8 	DMSO, H_2O, LiCl, 150°, 4 h	 (—) +  (—)	1110

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMF, H_2O, NaCl, 130–140°, 18 h	 (100)	1111
$C_{9–11}$  A: R^2 =  B: R^2 = 	Krapcho	 (see table below)	98
C_9 	DMSO, H_2O, NaCl, 155°, 10 h	 R: Bn (90); PMB (99)	1112
	DMSO, H_2O, NaCl, 160°, 6 h	 R: Bn (81); 2-Br-4,5-(OCH_2O)$C_6H_2CH_2$ (87)	1113; 1113, 278, 1114

R^1	R^2		er	Config.
n-Bu	A	(80)	72.5:27.5	(*R*)
n-Bu	B	(92)	73.5:26.5	(*S*)
c-C_6H_{11}	A	(84)	99.0:1.0	(*S*)
Ph	A	(98)	89.5:10.5	(*S*)
Ph	B	(87)	90.0:10.0	(*R*)
3-$O_2NC_6H_4$	A	(70)	88.5:11.5	(*S*)
4-$O_2NC_6H_4$	B	(80)	87.5:12.5	(*R*)
2-$MeOC_6H_4$	A	(84)	68.5:31.5	(*S*)
3-$MeOC_6H_4$	A	(76)	83.5:16.5	(*S*)
3,4-$(MeO)_2C_6H_3$	A	(84)	75.0:25.0	(*S*)
3,4-$(MeO)_2C_6H_3$	B	(96)	76.0:24.0	(*R*)

TABLE 8B. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTAMS (*Continued*)

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12} 	DMSO, H_2O, NaCl		1115
C_{11}  94.0:6.0 er	DMSO, H_2O, NaCl, 160°, 2 h	 (97)	1116
C_{12} 	DMF, H_2O, NaCl, reflux, overnight	 (71)	1117
	DMSO, H_2O, 180°, 2 h	 (59)	1118

R	Temp (º)	Time (h)	I	II	III
Ph	150	28	(—)	(0)	(0)
PMP	170	19	(0)	(23)	(72)
Bn	150	28	(—)	(0)	(0)

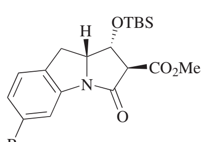
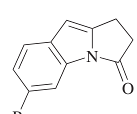
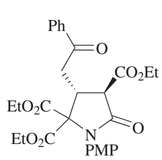
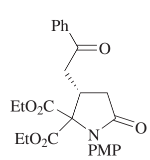
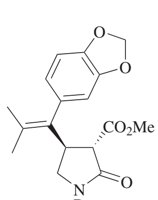
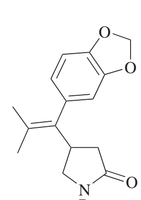
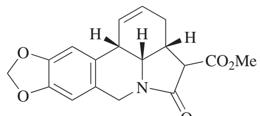
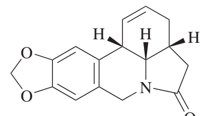
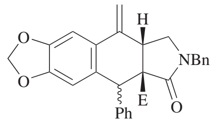
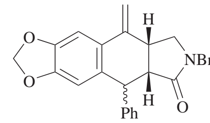
α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
	Krapcho	 R: H (—); MeO (—)	241
C_{15} 	DMF, 110°, 72 h	 (60)	183
	DMSO, H_2O, NaCl, Mw, 200°, 1 h	 (92)	1119
C_{16} 	DMSO, H_2O, NaCl, 175°, 12 h	 (93)	278, 1113, 1114

TABLE 8B. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED α-ALKOXYCARBONYL LACTAMS (*Continued*)

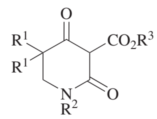
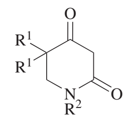
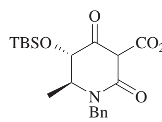
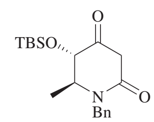
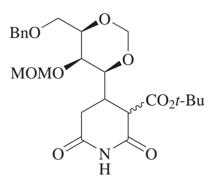
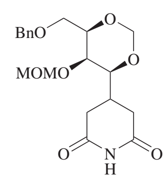
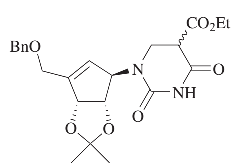
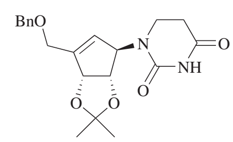
α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}  E = CO_2Me	DMSO, H_2O, NaCl, 160°, 5 h	 (57) 3 isomers, 71:21:8 [c]	1120

[a] The yield includes that of the preparation of the precursor.

[b] The following conditions led to decomposition: 1,2-propanediol, NaOMe; $Ba(OH)_2$•$2H_2O$, heat; DMSO, H_2O, LiCl, heat; TMSI.

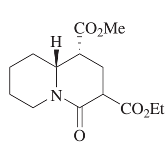
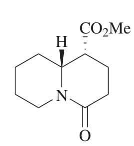
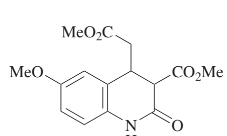
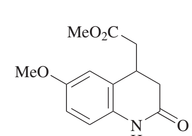
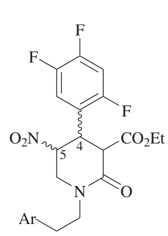
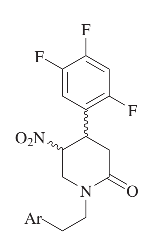
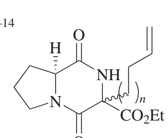
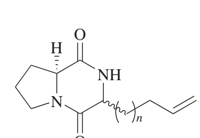
[c] The two major isomers were *cis*-fused.

TABLE 8C. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED α-ALKOXYCARBONYL LACTAMS

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-8} 	See table.		
C_7 	MeCN, H_2O, reflux, 2 h	 (—)	1124
C_{10} 	DMSO, H_2O, NaCl, 160–170°, 1 h	 (63)	94
C_{11} 	DMSO, H_2O, NaCl, reflux, 1 h	 (83)	1125

R^1	R^2	R^3	Solvent	Temp	Time (h)		Refs.
H	H	Me	MeCN, H_2O	reflux	4	(90)	1121
H	c-C_6H_{11}	Me	$MeNO_2$, H_2O	98°	1	(93)	1122
Me	H	Et	MeCN, H_2O	reflux	2	(—)	1123

TABLE 8C. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED α-ALKOXYCARBONYL LACTAMS (*Continued*)

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl, 130°, 72 h	 (72)	1126
C_{12} 	DMSO, H_2O, NaCl, 150–160°	 (—)	1127
	DMSO, H_2O, NaCl, 140°, overnight		1128
C_{13-14} 	DMF, H_2O, LiCl, 92°, 16 h		182

Ar	Config.	
3,4-(OCH_2O)C_6H_3	(4*R*,5*R*)	(61)
3,4-(OCH_2O)C_6H_3	(4*S*,5*S*)	(—)
3-$HO_2CC_6H_4$	(4*R*,5*R*)	(—)
3-MsC_6H_4	(4*R*,5*R*)	(—)
4-MsC_6H_4	(4*R*,5*R*)	(—)

n	
2	(74)
3	(74)

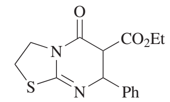
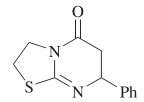
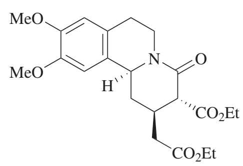
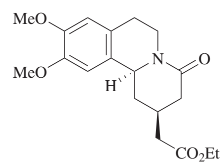
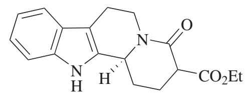
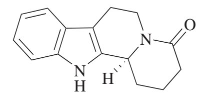
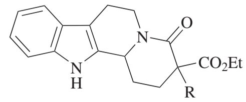
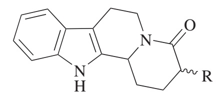
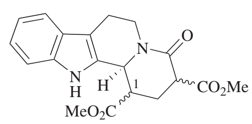
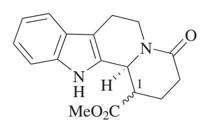
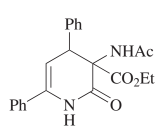
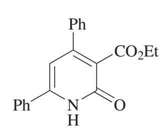
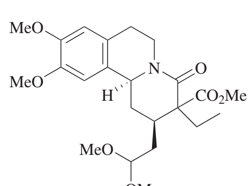
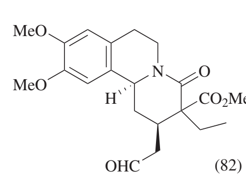
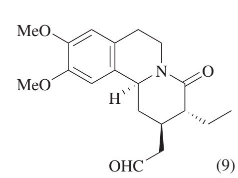
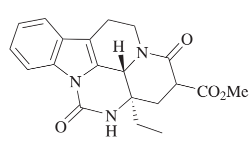
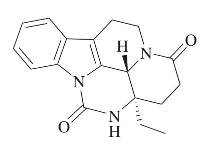
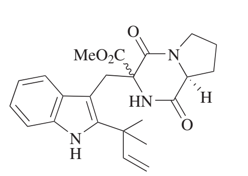
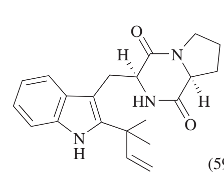
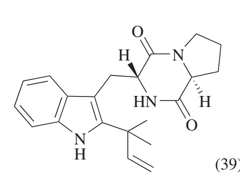
C_{13} 	DMSO, NaCl, 160°, 6 h	 (50)	1129
C_{16} 	DMSO, H_2O, NaCl, heat	 (47)	1130
	DMSO, H_2O, LiCl, 160°, 3.5 h	 (73)	1131
C_{16-18} 	DMSO, H_2O, LiCl, reflux, 4 h	 R H (89) Et two diastereomers: (51) + (23)	1132
C_{17} 	DMSO, LiI•3H_2O, 132°, 36 h	 C-1 Config. α (56) β (53)	1133

TABLE 8C. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED α-ALKOXYCARBONYL LACTAMS (*Continued*)

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	DMSO, NaCl, 160°, 4 h	 (60)	1134
	DMSO, H_2O, NaCl, 180–190°, 2 h	 (82) +  (9)	246
C_{19} 	DMF, LiI, reflux, 3.5 h	 (79)	1135
C_{22} 	DMSO, $MgCl_2$•2H_2O, 130–140°, 2.5 h	 (59) +  (39)	1136

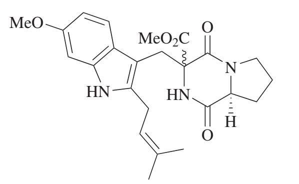
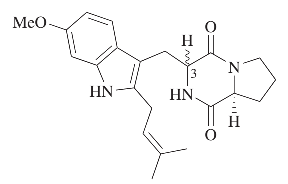
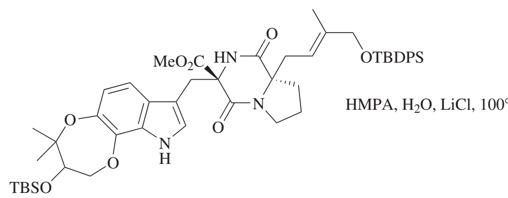
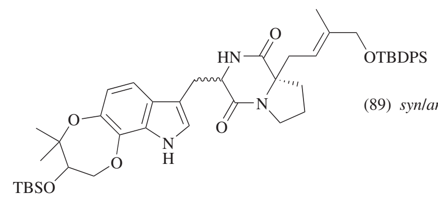
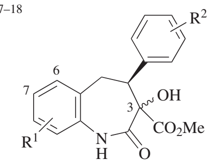
	DMSO, H_2O, LiCl, 160°, 0.5 h		H-3 α (40) + H-3 β (30)	1136a
	HMPA, H_2O, LiCl, 100°		(89) *syn*/*anti* = 3:1	1137

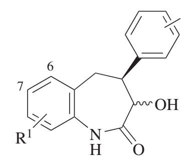
TABLE 8D. DEALKOXYCARBONYLATIONS OF SEVEN- AND HIGHER-MEMBERED α-ALKOXYCARBONYL LACTAMS

α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{17-18}

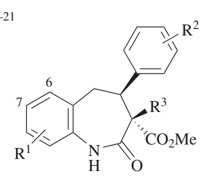


Pyridine, H_2O, LiI, reflux

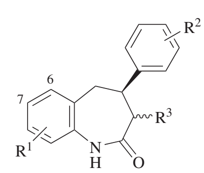


R^1	R^2	Time (h)		*cis/trans*	Refs.
H	4-MeO	1	(83)	82:18	1138, 1139
6-Cl	4-MeO	—	(8)[a]	—	1139
7-Cl	2-MeO	—	(70)[a]	—	1139
7-Cl	3-MeO	—	(61)[a]	—	1139
7-Cl	4-MeO	—	(59)[a]	—	1139
7-Br, 6-MeO	4-MeO	—	(52)[a]	—	1139
6-O_2N	4-MeO	—	(7)[a]	—	1139
6-MeO	4-MeO	—	(17)[a]	—	1139
6-CHF_2O	4-MeO	—	(22)[a]	—	1139
7-PhO	4-MeO	—	(6)[a]	—	1139
7-BnO	4-MeO	—	(18)[a]	—	1139
7-*t*-BuS	4-MeO	—	(61)[a]	—	1139
7-PhS	4-MeO	1.5	(95)	—	1139
6-Me	4-MeO	—	(15)[a]	—	1139
6-CF_3	4-MeO	—	(39)[a]	—	1139
7-CF_3	4-MeO	2	(78)	60:40	1140, 1139
6-NC	4-MeO	—	(33)[a]	—	1139
6-EtO_2C	4-MeO	—	(20)[a]	—	1139

C_{18-21}

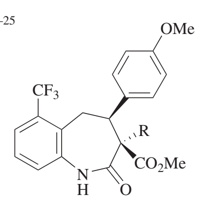


See table.

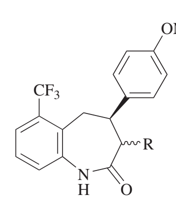


R^1	R^2	R^3	Solvent	Additive(s)	Temp (º)	Time (h)		*cis/trans*	Refs.
H	4-MeO	Me	pyridine	LiI	—	—	(—)	50:50	1138, 1139
H	4-MeO	Me	DMF	LiBr, 4-$HSC_6H_4NH_2$[b]	137	5	(94)	>97:3	1138
H	4-MeO	allyl	DMF	LiBr	142	—	(22)[a]	—	1139
7-Br, 6-MeO	4-MeO	Me	DMF	LiBr	142	—	(26)[a]	—	1139
6-MeO	4-MeO	Me	DMF	LiBr	142	—	(24)[a]	—	1139
6-CF_3	4-MeO	H	DMF	LiBr	142	—	(2)[a]	—	1139
6-CF_3	3,4-$(MeO)_2$	Me	DMF	LiBr	142		(38)[a]	—	1139
6-CF_3	4-MeS	Me	DMF	LiBr	142	—	(36)[a]	—	1139
6-CF_3	4-Et	Me	DMF	LiBr	142	4	(76)	97:3	1139

C_{19-25}



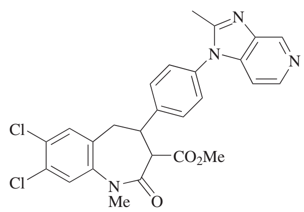
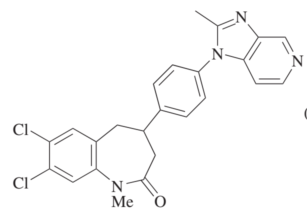
DMF, LiBr,
4-$HSC_6H_4NH_2$[b],
135º, 5 h



R		*cis/trans*
Me	(93)[c]	95:5
Et	(100)	90:10
allyl	(85)	87:13
Bn	(100)	50:50

48, 1139

TABLE 8D. DEALKOXYCARBONYLATIONS OF SEVEN- AND HIGHER-MEMBERED α-ALKOXYCARBONYL LACTAMS (*Continued*)

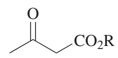
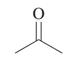
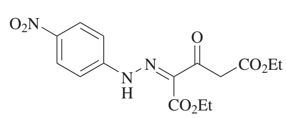
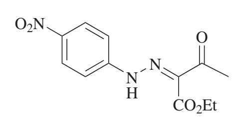
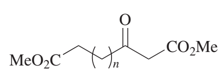
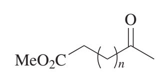
	α-Alkoxycarbonyl Lactam	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24}		DMF, pyridine, reflux, 2 h	 (75)	1141

[a] The yield is that of the *cis* isomer and includes the preparation of the precursor.

[b] The addition of 4-aminothiophenol was required to trap the methyl bromide which otherwise caused *N*-methylation as a side reaction.

[c] The reaction was also carried out with the (3*S*)-enantiomer: the yield and selectivity were the same.

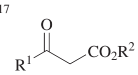
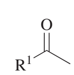
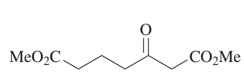
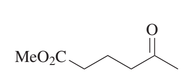
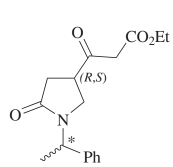
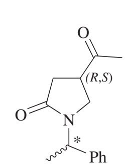
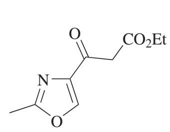
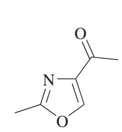
TABLE 9A. DEALKOXYCARBONYLATIONS OF ACYCLIC α-UNSUBSTITUTED β-KETO ESTERS

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	See table.		
C_5 	H_2O, reflux, 3 d	 (—)	1145
$C_{6–7}$ 	$B(OH)_3$, 110°		1146

R	Solvent	Additive	Temp (°)	Time (h)		Refs.
Me	H_2O	—	105–120	—	(—)	1154
Et	—	NaI	150–160	7	(24)	1142
Et	—	NaI•$2H_2O$	150–160	2.5	(56)	1143
Et	$HO(CH_2)_2OH$	NaI	150–160	4	(34)	1142
Et	PhOH	NaI	150–160	4	(30)	1142
Et	—	CaI_2	130–150	2	(36)	1142
Et	—	CaI_2•$4H_2O$	144–155	2	(60)	1143
Et	$HO(CH_2)_2OH$	CaI_2	130–150	2	(57)	1142
Et	PhOH	CaI_2	130–150	2	(35)	1142
Et	—	$B(OH)_3$	150	—	(0)	329
Et	H_2O	—	200	9	(97)	1144, 19
c-C_6H_{11}	—	$B(OH)_3$	150	—	(90)	329

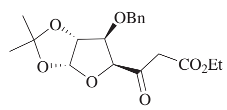
n	
1	(—)
2	(—)

TABLE 9A. DEALKOXYCARBONYLATIONS OF ACYCLIC α-UNSUBSTITUTED β-KETO ESTERS (*Continued*)

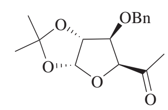
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{7–17}$ 	See table.	 (—)	
C_7 	$B(OH)_3$, 150–170°, 2.5 h	 (53)	1149
	DMSO, H_2O, additive, 130–135°		
	Xylenes, DABCO, reflux, 45 min	 (63)	1152

R^1	R^2	Solvent	Additive	Temp (°)	Time (h)		Refs.
n-Bu	Me	—	—	270[a]	—	(—)	1147
t-Bu	Me	H_2O	—	105–120	—	(—)	19
t-Bu	Et	H_2O	—	105–120	—	(—)	19
n-C_9H_{19}	Et	xylenes	DABCO	reflux	5	(—)	1148
n-$C_{10}H_{21}$	Et	xylenes	DABCO	reflux	5	(—)	1148
n-$C_{11}H_{23}$	Et	xylenes	DABCO	reflux	5	(—)	1148
n-$C_{12}H_{25}$	Et	xylenes	DABCO	reflux	5	(—)	1148
n-$C_{13}H_{27}$	Et	xylenes	DABCO	reflux	5	(—)	1148
n-$C_{14}H_{29}$	Et	xylenes	DABCO	reflux	5	(—)	1148

* Config.	Additive	Time (h)		Refs.
(*R*)	LiCl	1.5	(—)	1150
(*S*)	NaCl	20	(36) + (33)[b]	1151

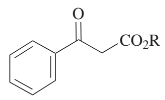


DMSO, H_2O, NaCl, 135°, 2 h

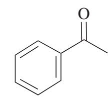


(80) 1153

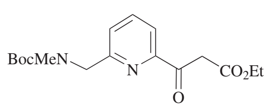
C_9



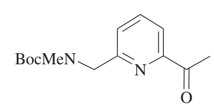
See table.



R	Solvent	Additive(s)	Temp (°)	Time		Refs.
Me	H_2O	—	200	0.5 h	(73)	1154
Et	H_2O	—	reflux	—	(—)	1155, 1156
Et	H_2O	—	Mw, 160	3 min	(82)	17
Et	dioxane	H_2O, Al_2O_3	reflux	16 h	(89)	310
Et	diglyme	H_2O	105	16 h	(70)	19
Et	xylenes	DABCO	reflux	5 h	(—)	1148
Et	DMSO	H_2O	reflux	4 h	(70)	15
Et	DMSO	$MgCl_2$	150	1 h	(41)[c]	109



Dioxane, H_2O, Al_2O_3, reflux

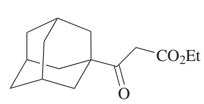


(27) 1157

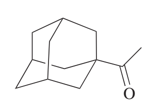
TABLE 9A. DEALKOXYCARBONYLATIONS OF ACYCLIC α-UNSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.

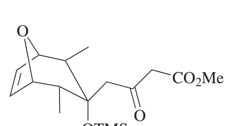
C_{13}



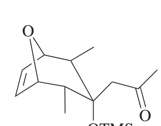
o-Xylene, additive, reflux



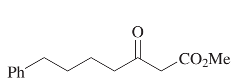
Additive	Time (h)		Refs.
DABCO	6	(84)	297
3-quinuclidinol	6	(88)	294
brucine	24	(49)	883
tropine	24	(2)	883
nicotine	24	(81)	883
reserpine	24	(8)	883
yohimbine•HCl	24	(90)	883
quinidine	24	(12)	883
quinine•H_2O	6	(79)	882
perloline•HCl	6	(95)	882



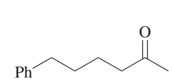
DMSO, H_2O, NaCl, reflux, 3 h



(40) 1158

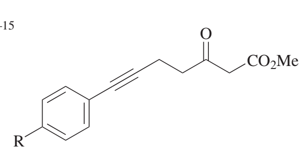


PhMe, DMAP, phosphate buffer, 90°, 1 d

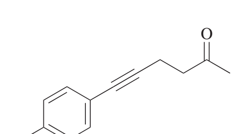


(68) 87

C_{13-15}

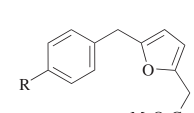


DMF, K_2CO_3, 100°, 6 h



I

\+



II

1159

R	I	II
MeO	(51)	(0)
MeCO	(0)	(51)

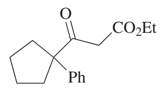
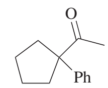
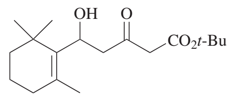
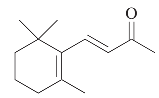
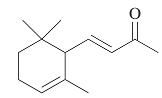
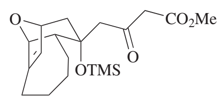
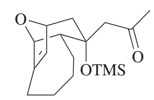
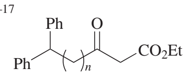
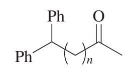
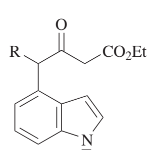
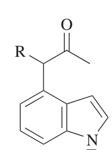
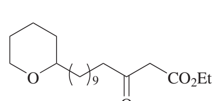
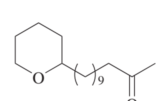
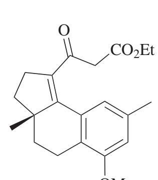
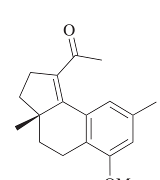
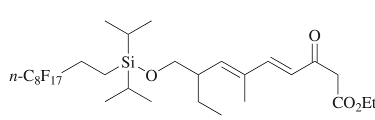
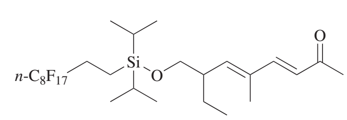
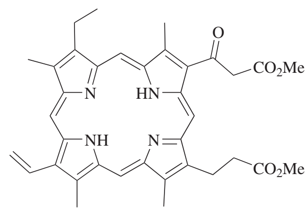
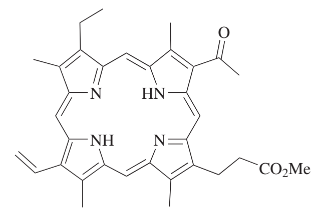
C_{14} 	Xylenes, DABCO, reflux, 5 h		(—)	1148
	DMSO, H_2O, LiCl, 180°, 1 h	 **I** +  **II**	**I + II** (47), **I/II** = 7:3	1160
C_{15} 	DMSO, H_2O, NaCl, reflux, 3 h		(50)	1158
C_{16-17} 	Xylenes, DABCO, reflux, 5 h		*n* 0 (—); 1 (—)	1148

TABLE 9A. DEALKOXYCARBONYLATIONS OF ACYCLIC α-UNSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{16} 	DMF, LiCl		R: *i*-Bu (—); CH_2=C(Me)CH_2 (—)	1161
C_{18} 	Xylenes, DABCO, reflux, 5 h		(40)	1148
	DMF, H_2O, LiI, 140°, 1 h		(98)	1162
C_{22} 	DMF, H_2O, Mw, 160°, 3 min		(89)	17

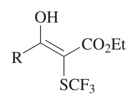
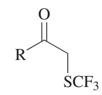
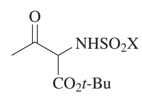
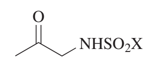
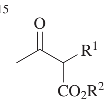
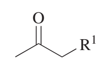
C_{34} 	PhMe, DMAP, phosphate buffer, 90°, 12 h			(75)	1163

[a] The substrate was injected into the preheater of a gas chromatograph.

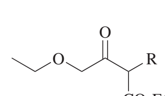
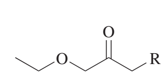
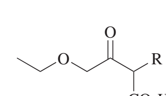
[b] The product was a 1:1 mixture of diastereomers. The numbers are the yields of the individual diastereomers isolated by chromatography.

[c] The yield is that of the tosylhydrazone.

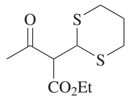
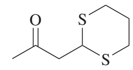
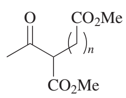
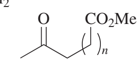
TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-9} 	DMSO, H_2O, reflux, 4 h	 R: Me (44); Ph (66)	1164
C_4 	100°	 X: F (85); Cl (75)	1165
C_{5-15} 	See table.		

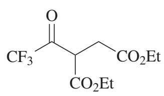
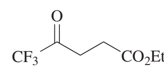
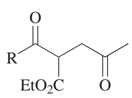
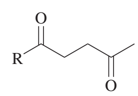
R^1	R^2	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
Me	Me	—	—	105	—	(—)	19
Me	Et	—	—	105	—	(—)	19
Me	Et	H_2O	—	250	0.5	(—)	1154
Me	Et	—	NaI	160–170	15	(15)	1142
Me	Et	—	NaI•$2H_2O$	150–160	3	(9)	1142
Me	Et	$HO(CH_2)_2OH$	NaI	160–170	8	(33)	1142
Me	Et	PhOH	NaI	160–170	8	(14)	1142
Me	Et	—	CaI_2	130–150	2	(36)	1142
Me	Et	—	CaI_2•$4H_2O$	145–155	1.5	(73)	1142
Me	Et	$HO(CH_2)_2OH$	CaI_2	130–150	2	(52)	1142
Me	Et	PhOH	CaI_2	130–150	2	(45)	1142
Me	Et	DMSO	H_2O, NaCl	reflux	4	(70)	15
Me	Et	1-oxo-1-methylphospholine	H_2O, NaCl	170–180	—	(92)	113
Et	Et	H_2O	—	250	0.5	(100)	1154
$EtO(CH_2)_2$	Et	H_2O	—	250	—	(—)	1166
n-Pr	Et	DMSO	H_2O, NaCl	153–165	5	(85–95)	333
$PhSe(CH_2)_3$	Et	DMF	H_2O, LiCl	170	18	(75)	767
n-Bu	Et	EtOH, PhH	KOH, 18-c-6	rt; then reflux	16; 2	(86)	330
$BnO(CH_2)_5$	Et	DMSO	H_2O, NaCl	165	6	(73)	422
(*E*)-CH_2=CHCH=$CH(CH_2)_2$	Me	DMF	H_2O, LiCl	reflux	—	(44)	1167
n-C_7H_{15}	Et	*o*-xylene	DABCO	reflux	4	(>96)	297
$HO(CH_2)_{10}$	Me	DMSO	H_2O, NaCl	150	18	(75)	1168
n-$C_7H_{15}CHMe(CH_2)_2$	Et	DMSO	H_2O	165	6	(75)	1169
$CH_2=CH(CH_2)_9$	Et	DMSO	H_2O, NaCl	reflux	10	(40)	1170

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-8}  I	H_2O, 210°, 1 h	 II +  III	1171

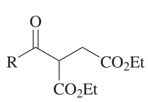
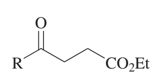
R	I	II	III[a]
Me	"some"	"low"	"some"
Et	"some"	"low"	"some"
n-Pr	—	—	"chiefly"
i-Pr	—	—	"chiefly"
i-Bu	—	—	"chiefly"

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	DMSO, NaCl	 (—)	1172
C_{6-14} 	A. 1. H_2O, 200° 2. H_2SO_4, MeOH, CH_2Cl_2 B. DMSO, H_2O, LiCl, 168°, 4 h C. DMF, PhSH, K_2CO_3, 85°, 3 h		

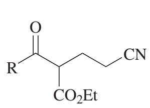
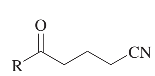
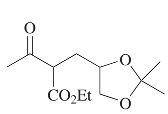
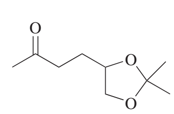
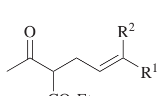
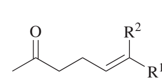
n	Cond.		Refs.
1	A	(35)	1147
2	A	(28)	1147
2	B	(73)[b]	1173
3	A	(33)	1147
4	C	(—)	1174
5	A	(30)	1147
9	A	(28)	1147

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$B(OH)_3$, slowly heated to 170°	 (62)	316
C_7 	See table.		

R	Solvent	Additives	Temp (º)	Time (h)		Refs.
Me	H_2O	—	160	"several"	"low"	1175
CF_3	DMSO	H_2O, NaCl	110	2.5	(73)	1176

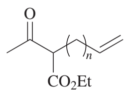
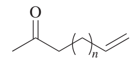
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-11} 	See table.		

R	Solvent	Additive	Temp (º)	Time (h)		Refs.
Et	DMSO	H_2O	reflux	4	(95)	314
Et	—	$B(OH)_3$	150	1.5	(82–85)	313, 312, 1177
n-Pr	—	$B(OH)_3$	150	1.5	(80)	312, 1177
n-C_6H_{13}	—	$B(OH)_3$	150	1.5	(80)	312

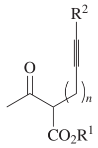
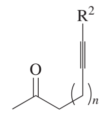
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-12} 	H_2O, Na_2CO_3, "heat"	 R: Me (66); *n*-Pr (78); Ph (—)	1178
C_7 	DMF, $(n\text{-Bu})_4N^+AcO^-$, 90–95°, 2 h	 (80)	1179
C_{7-8} 	DMSO, additive		

R^1	R^2	Additive	Temp (º)	Time (h)		Refs.
H	Cl	LiCl	—	—	(—)	1180
Me	H	H_2O	185	3	(57)	1181

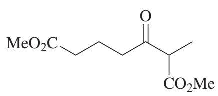
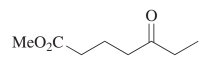
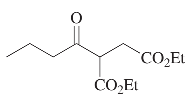
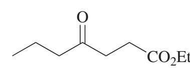
TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

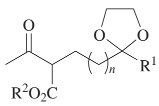
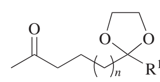
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-15} 	See table.		

n	Solvent	Additive	Temp	Time (h)		Refs.
2	—	—	—	—	(—)	1182
3	—	—	—	—	(—)	1183
9	DMF	LiI	reflux	12	(81)	1184

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	See table.		

n	R^1	R^2	Solvent	Additives	Temp (°)	Time (h)		Refs.
2	Et	TMS	HMPA	H_2O, LiCl	140	6	(65)	1185
3	Me	H	—	—	—	—	(56)	1186

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	$B(OH)_3$, 110°	 **I** (—)	1146
	270° [c]	**I** (—)	1147
	$B(OH)_3$	 (—)	1187

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	See table.		

n	R^1	R^2	Solvent	Additives	Temp (°)	Time (h)		Refs.
1	Me	Et	DMSO	H_2O, NaCl	160	8	(60)	1188
3	H	Me	DMF	K_2CO_3, PhSH	85	3	(—)	1174

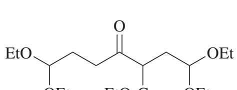
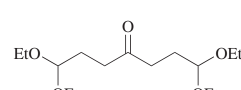
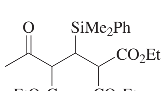
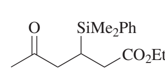
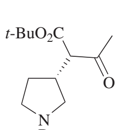
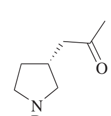
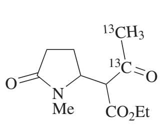
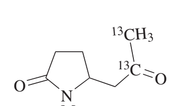
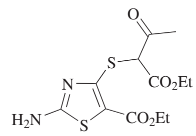
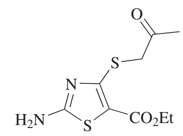
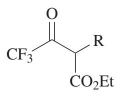
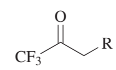
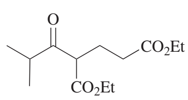
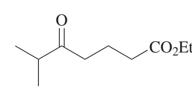
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	DMF, H_2O, NaCl, reflux, 72 h	 (88)	342
	DMSO, H_2O, NaCl, 125–160°, 38 h	 (61)	421, 1189
	DMF, H_2O, NaCl, reflux, 9 h	 (92)	1190
	DMF, H_2O, NaCl	 (91)	1191

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	DMSO, H_2O, NaCl, 150°, 5 h	 (47)	1192
C_{9-16} 	DMF, H_2O, LiCl, reflux, 1–2 h	 R $Me_2C{=}CHCH_2$ (62) Bn (85) n-C_8H_{17} (65) $Ph(CH_2)_2$ (85) $Ph(CH_2)_3$ (90) $PhCH{=}CHCH_2$ (77) $CH_2{=}CPh(CH_2)_2$ (38) $MeC(Ph){=}CH(CH_2)_2$ (56) $CH_2{=}CPh(CH_2)_4$ (44) $MeC(Ph){=}CH(CH_2)_3$ (52)	1193, 1194, 1195
C_9 	DMSO, H_2O, NaCl	 (70)[b]	1196

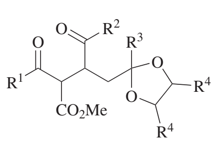
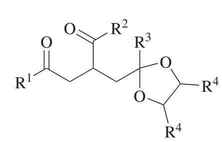
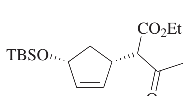
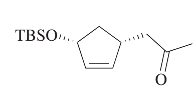
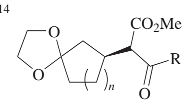
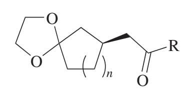
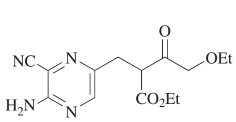
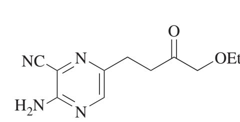
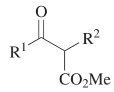
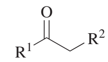
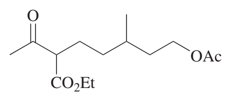
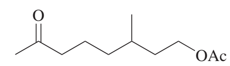
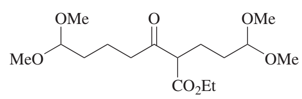
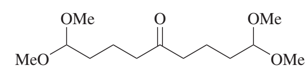
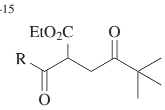
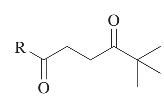
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-12} 	DMSO, H_2O, NaCl, 160–180°, 8 h	 R^1 R^2 R^3 R^4 Me Me H Me (45) Me Me Me H (44) Me Et Me H (44) Me n-Pr Me H (46) Et Me H Me (42)	1197
C_9 	DMSO, H_2O, NaCl, reflux	 (85)	1198
C_{9-14} 	Xylene, DABCO, 140°, 24 h	 (—) n = 1; R = Me, Et, n-Pr, $CH_2{=}CH(CH_2)_2$ n = 2; R = Me, Et, n-Pr, n-Bu, $CH_2{=}CH(CH_2)_2$, $CH{\equiv}C(CH_2)_2$, c-C_5H_9 n = 3; R = Me, Et, $CH_2{=}CH(CH_2)_2$, $CH{\equiv}C(CH_2)_2$	449
C_9 	DMSO, H_2O, NaCl, 150–160°, 5 h	 (21)	473

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-15} 	See table.		

R^1	R^2	Solvent	Additives	Temp (°)	Time (h)		Refs.
n-C_6H_{13}	Me	H_2O	—	210	2	(94)	1200
Et	$Me_2CH(CH_2)_4$	DMSO	H_2O, NaCl	reflux	24	(88)	1199
n-$C_{11}H_{23}$	Me	PhMe	DMAP, phosphate buffer (pH 7)	90	6	(0)	87

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	DMF, LiI, reflux, 12 h	 (81)	1184
	DMF, H_2O, NaCl, reflux, 35 h [d]	 (67)[b]	275
C_{10-15} 	DMSO, H_2O, NaCl, 160°, 20 h	 R: Me (75); n-Pr (83); t-Bu (48); Ph (60)	1201

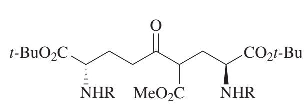
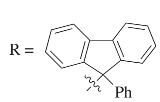
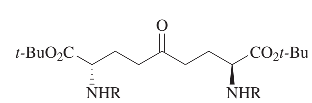
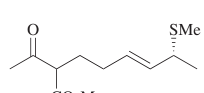
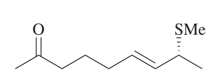
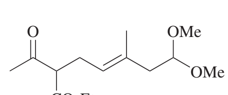
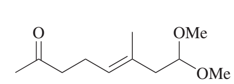
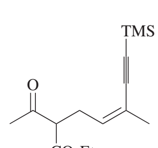
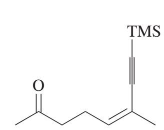
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}  	DMSO, H_2O, 160°	 (0)[e]	1202
	DMSO, H_2O, NaCl, 70°, 12 h	 (80)	1203
	DMSO, H_2O, NaCl, 160°, 9 h	 (55)	1204
	DMSO, H_2O, NaCl, 190°	 (—)	1205

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

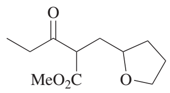
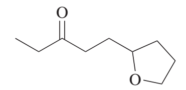
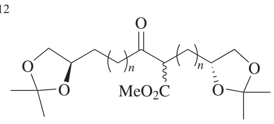
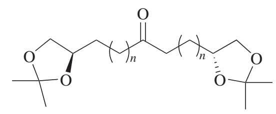
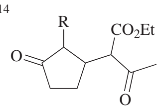
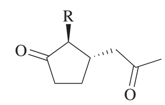
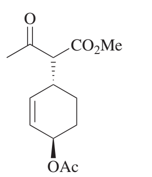
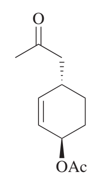
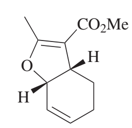
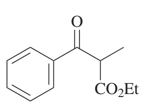
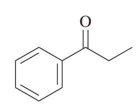
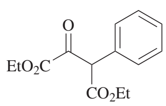
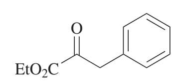
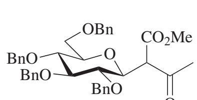
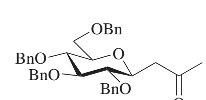
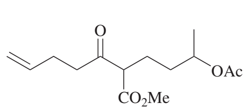
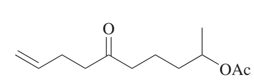
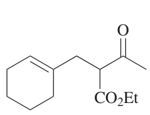
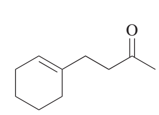
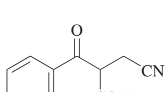
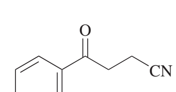
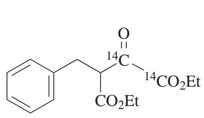
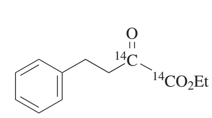
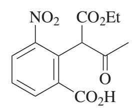
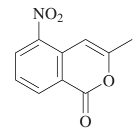
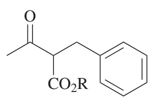
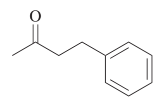
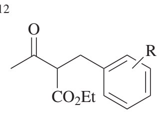
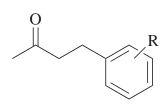
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	DMF, Na_2CO_3, reflux, 3 h	 (78)	1206
C_{10-12}			
	DMSO, H_2O, LiCl, reflux	 *n* | Time (min) 1 | 5 | (92) 2 | 10 | (94)	1207
C_{10-14}			
	H_2O, 180°, 4 h	 R | | Config. Me | (58) | racemic *n*-C_5H_{11} | (58) | (*S*,*S*)	1208
C_{10}			
	DMSO, H_2O, LiCl, 175°, 45 min	 (60) +  (8)	198
	20% HCl/EtOH, reflux; or 150°, steam distillation	 (—)	1209
	DMSO, H_2O, NaCl, 130°, 90 min	 (—)	1210
	DMF, PhSH, K_2CO_3, reflux, 2 h	 (80)	525
C_{11}			
	DMSO, H_2O, NaCl, reflux, 12 h	 (51)	1211
	DMSO, H_2O, NaCl, 140–150°, 10 h	 (92)	1212
	H_2O, $BnNH_2$, rt, 3 h	 (10)	1213
	DMSO, H_2O, NaCl, 135°, 3 h	 (93)	1214

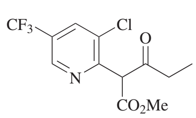
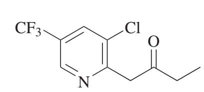
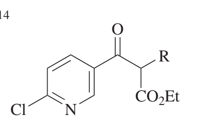
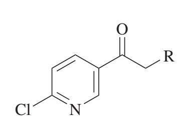
TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, 170°, 4 h	 (58)	200
	See table.		

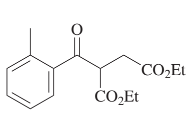
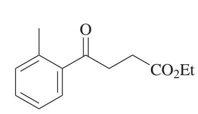
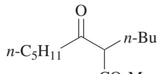
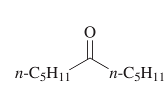
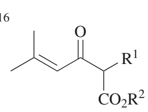
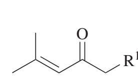
R	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
Me	DMF	Cs_2CO_3, 4-$H_2NC_6H_4SH$	85	3	(98)	304
Me	n-$C_{17}H_{35}CO_2H$	(n-Bu)$_4$PBr	200	16	(72)	321
Et	H_2O	—	200	8	(97)	1144, 1154
Et	DMSO	H_2O, NaCl	170	—	(—)	1215
Et	DMF	Cs_2CO_3, 4-$H_2NC_6H_4SH$	85	20	(37)	304
Et	$EtCO_2H$	—	reflux	24	(90)	322
Et	n-$C_{17}H_{35}CO_2H$	(n-Bu)$_4$PBr	200	16	(76)	321

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12} 	DMSO, H_2O, NaCl, 170°		

R	Time (h)		Refs.
2-Cl	—	(—)	1215
2-Br	—	(—)	1215
3,4-Cl_2	—	(—)	1215
2-Me	7	(63)[b]	1216

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl, 130°, 8 h	 (39)	1783
C_{11-14} 	DMSO, H_2O, 155°, 3 h		1217

R	
c-Pr	(—)
Ph	(56)
4-ClC_6H_4	(—)
4-$Me_2NC_6H_4$	(—)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	DMSO, H_2O, NaCl, 140–160°, 4 h	 (78)	162
	Dioxane, H_2O, basic Al_2O_3, reflux, 29 h	 (95)	310
C_{12-16} 	Krapcho		1218

R^1	R^2	
n-C_5H_{11}	Me	(85)
Ph	Et	(70)
4-MeC_6H_4CHMe	Et	(69)

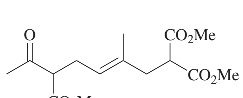
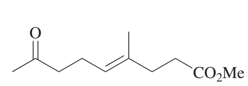
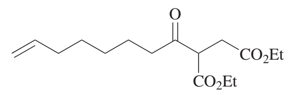
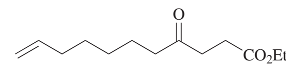
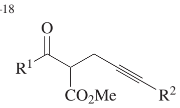
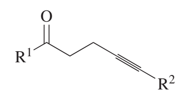
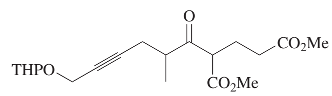
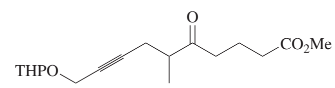
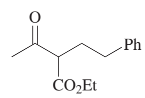
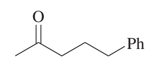
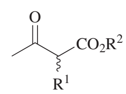
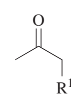
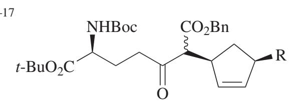
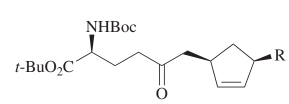
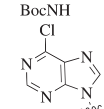
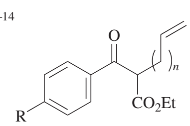
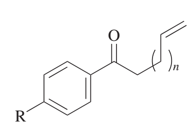
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	DMSO, H_2O, LiCl, 170°, 45 min	 (65)	85

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	B_2O_3, 150°, 1 h; 175°	 (87)	317
C_{12-18} 	DMSO, H_2O, LiCl, reflux, 10 h	 (74-90) R^1 / R^2: Me / Ph; Ph / H; Ph / TMS; Ph / Ph	352, 360
C_{12} 	Krapcho	 (—)	1219
	Krapcho	 (—)	1183
 "low er"	DMSO, LiCl; or EtOH, KOH	 (—) R^1 / R^2: 2-octyl / (–)-menthyl; PhCHMe / (–)-menthyl; 2-octyl / (–)-phenylmenthyl; PhCHMe / (–)-phenylmenthyl; 2-octyl / (+)-menthyl	1220

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-17} 	THF, H_2O, Na_2S•$9H_2O$, rt, 60 h	 R: BocNH (78);  (71)	1221
C_{12-14} 	See table.		

R	*n*	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
H	1	DMF	H_2O, LiBr	190–200	72	(78)	1222
H	1	xylene	DABCO	180	5	(—)	1223
Cl	1	DMF	H_2O, LiBr	190–200	72	(75)	1222
Br	1	DMF	H_2O, LiBr	190–200	72	(60)	1222
O_2N	1	xylene	DABCO	180	5	(89)	1223
MeO	1	DMF	H_2O, LiBr	190–200	72	(72)	1222
Me	1	DMF	H_2O, LiBr	190–200	72	(67)	1222
H	2	DMF	H_2O, LiBr	190–200	72	(77)	1222
H	3	DMF	H_2O, LiBr	190–200	72	(77)	1222

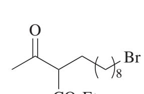
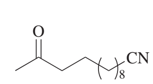
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	DMSO, H_2O, NaCN, 160–165°, 3 h	 (28)	1224

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

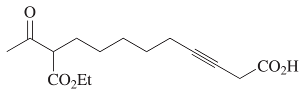
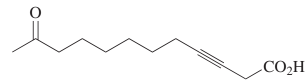
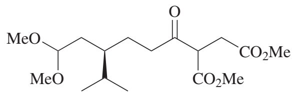
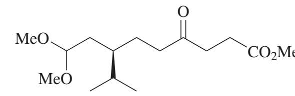
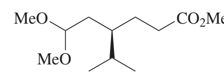
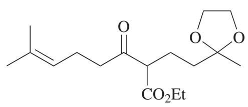
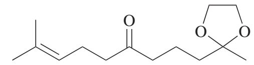
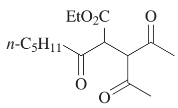
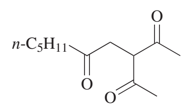
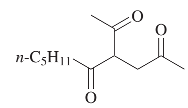
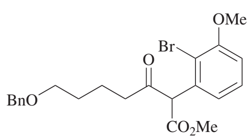
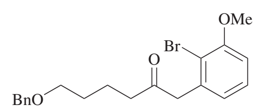
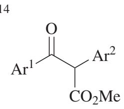
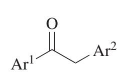
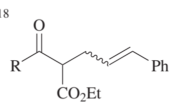
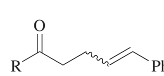
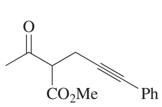
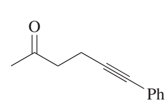
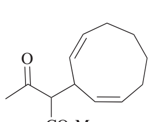
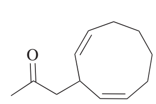
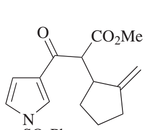
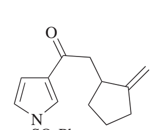
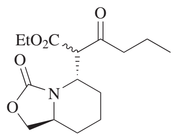
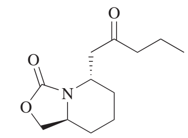
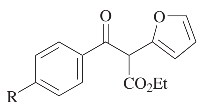
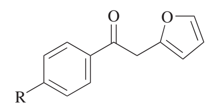
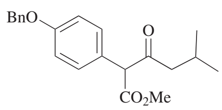
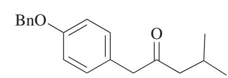
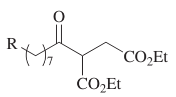
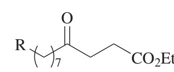
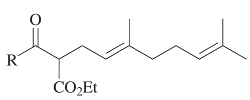
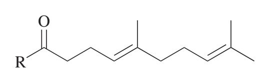
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	DMF, H_2O, LiCl, 170°, 30 min	 (—)	1225
	DMSO, H_2O, NaCl, 140°, 9 h	 (34) +  (—)[f]	196
	DMSO, H_2O, NaCl, 170°, 8 h	 (70)	1226
	DMSO, H_2O, NaCl, 140°, 4 h	 **I** +  **II**[g] **I** + **II** (—), **I**/**II** = 1:1	201
	DMSO, H_2O, NaCl, 140°, 2 h	 (90)	1227
C_{13-14}			
	DMSO, H_2O, NaCl, 150°, 2 h	 Ar^1 / Ar^2 4-pyridazinyl / 4-$MeOC_6H_4$ (2) 4-pyridyl / 4-FC_6H_4 (21) 4-pyridyl / 4-$MeOC_6H_4$ (87)	215, 1228
C_{13-18}			
	DMSO, H_2O, LiCl, reflux, 10 h	 R Me (79) Ph (77)	1230
C_{13}			
	HMPA, H_2O, LiCl, 140°, 6 h	 (—)	1231
	DMSO, H_2O, 180°	 (99)	1232
	HMPA, $MgCl_2$, 140–150°, 2 h	 (78)	1233

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	EtOH, H_2O, K_2CO_3, 90°, 12 h	 (91)	1234
	See table.		
		R — Cond.	
		H — NMP, HOAc, LiCl, reflux, 1 h (86)	432
		MeO — NMP, H_2O, HOAc, LiCl, 130° (82)	1235
	DMSO, H_2O, NaCl, 150°	 (96)	1236
C_{14}			
	B_2O_3	 R: CH_2=CH (—); Et (—)	1237
	DMF, H_2O, LiCl, reflux, 4 h	 R: CHF_2 (50); CF_3 (68)	1238

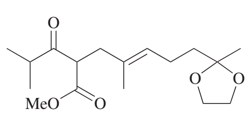
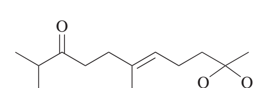
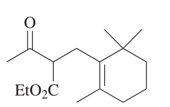
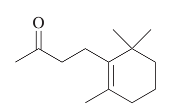
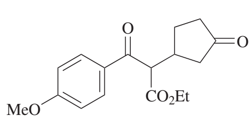
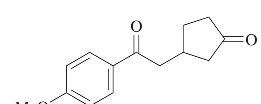
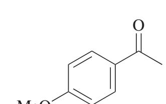
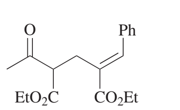
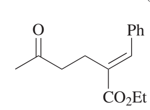
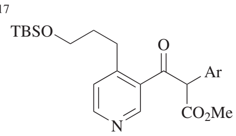
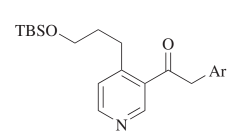
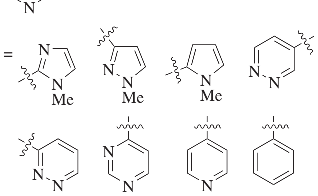
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, LiCl, pyridine, 185°, 5 h	 (63)	583
	Krapcho	 (—)	1239
	DMSO, H_2O, NaCl	 (—) +  (—)	195
	*p*-Xylene, DMAP, 120°, 4 d	 (64)	299
$C_{14–17}$			
	DMSO, H_2O, NaCl, 150°	 (—)	1240
		Ar = 	

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

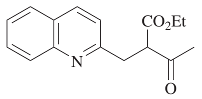
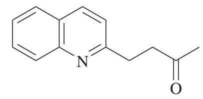
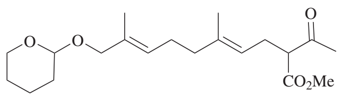
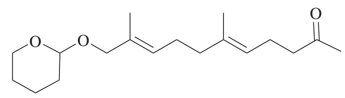
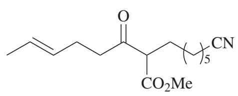
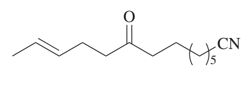
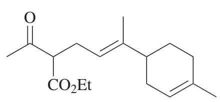
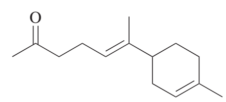
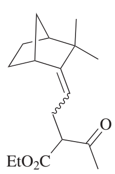
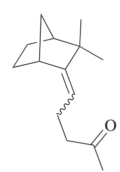
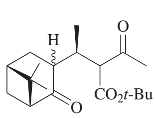
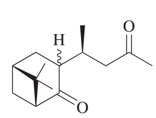
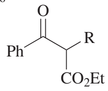
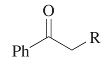
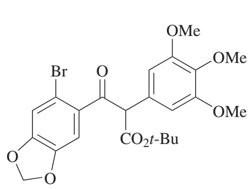
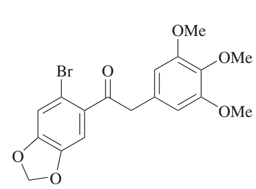
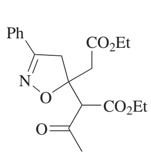
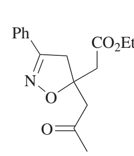
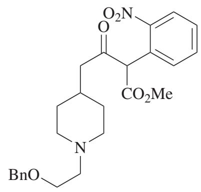
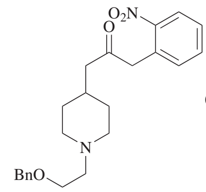
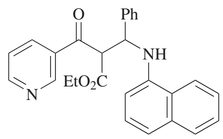
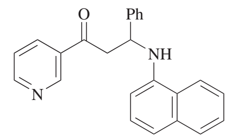
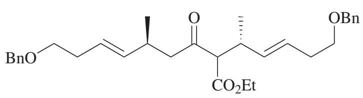
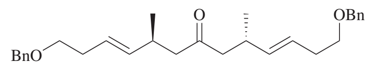
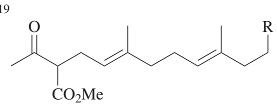
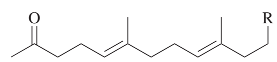
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	H_2O, 200°, 18 h	 (70)	1241
	DMSO, H_2O, NaCl, 150°, 4 h	 (70)	1242
C_{15}			
	DMSO, H_2O, LiCl, reflux, 3.5 h	 (76)	1243
	DMSO, H_2O, NaCl, 140°	 (38)	1244
	DMSO, H_2O, NaCl, 140–150°, 10 h	 (41)	1245
	DMSO, H_2O, NaCl, 160°, 20 h	 (88) 3:2 dr	1246
C_{15-16}			
	DMF, H_2O, Mw, 200°, 20 min	 R: n-C_6H_{13} (84); Bn (91)	17
C_{15}			
	DMSO, H_2O, heat	 (74)[b]	1247
	Xylene, DMAP, reflux, overnight	 (62)	300

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	DMSO, H_2O, LiCl, 155–160°, 3 h	 (85)	185
	Toluene, piperidine, reflux, 3 h	 (18)	303
C_{16}			
	DMSO, H_2O, LiCl, 190°, 40 min	 (96)	187, 1248
C_{16-19}			
	DMSO, H_2O, additive, reflux, 3 h	 R / Additive: MeO_2C NaCl (75); Me_2C=CH LiBr (80)	625; 1249

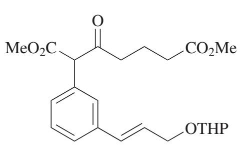
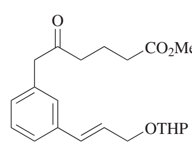
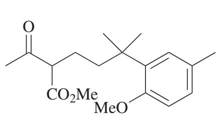
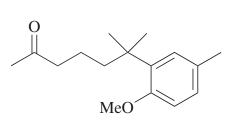
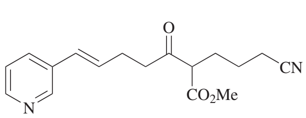
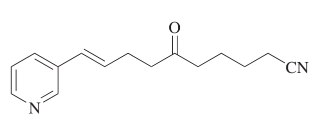
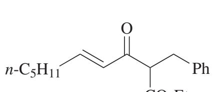
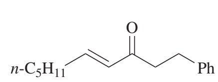
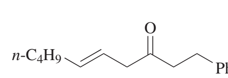
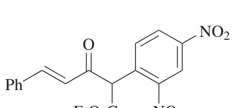
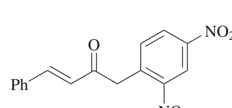
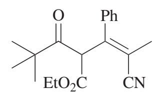
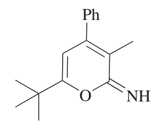
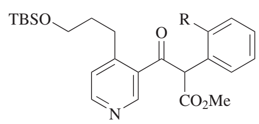
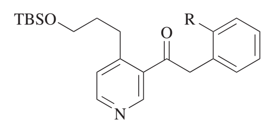
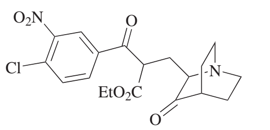
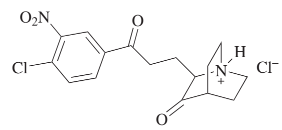
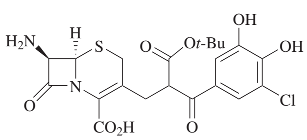
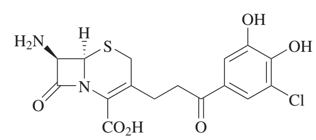
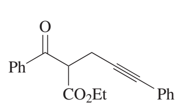
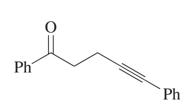
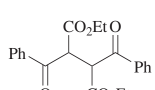
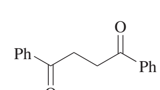
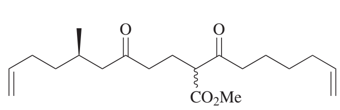
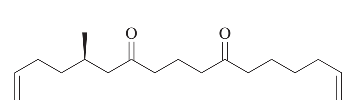
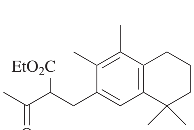
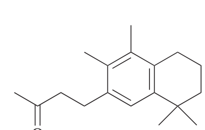
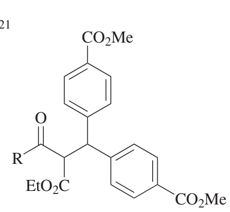
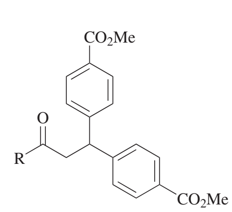
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	HMPA, H_2O, 190°, 15 min	 (90)	1250
	DMSO, H_2O, NaCl, reflux, 6 h	 (—)	1251
	DMSO, H_2O, NaCl, reflux, 14 h	 (93)	888
C_{17}			
	DMSO, H_2O, NaCl, 140°, 12 h	 (40) +  (13)	1252, 259
	H_2O, 120–130°, 5 h	 (—)	1253

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	DMSO, H_2O, NaCl, 150°, 20 h	 (34)	199
C_{17-18}			
	DMSO, H_2O, NaCl, 150°	 R / Time (h): H, 2, (70); Me, 0.5, (76)	1254
C_{17}			
	1. DMSO, H_2O, NaCl, 135°, 8 h 2. HCl, MeOH	 (82)	1255
	Sulfolane, BF_3•Et_2O[h], H_2O, 5°, 12 h	 (45)[b]	1256
C_{18}			
	DMSO, H_2O, LiCl, reflux, 10 h	 (74)	352
	H_2O, 150–170°	 (—)	1257
C_{19}			
	DMPU[i], LiCl, 120°, 7 h	 (72)	1258
	DMSO, H_2O, NaCN, 140–150°, 10 h	 (60)	1259
C_{19-21}			
	DMSO, H_2O, NaCl, 130–170°, 30 min	 R: Me (64); Et (53); *n*-Pr (56)	1260

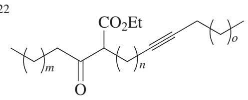
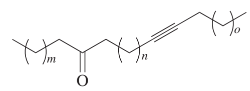
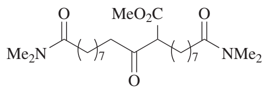
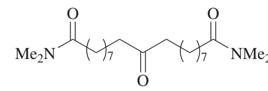
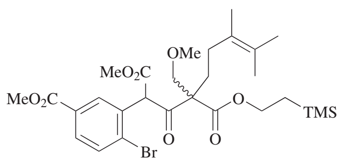
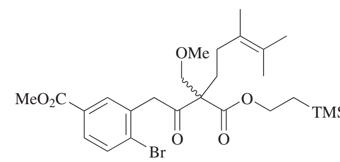
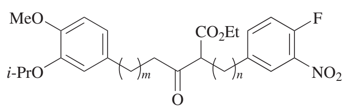
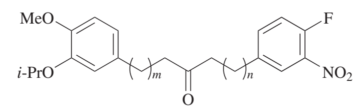
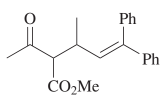
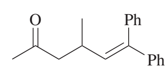
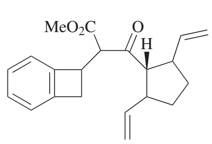
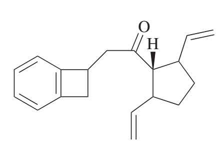
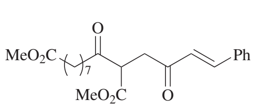
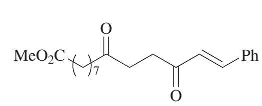
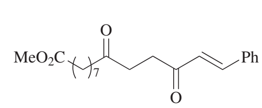
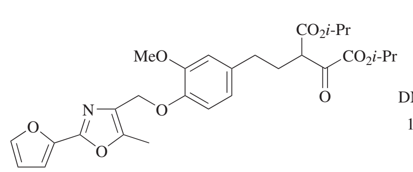
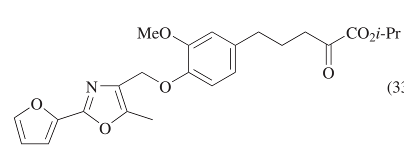
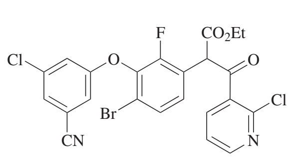
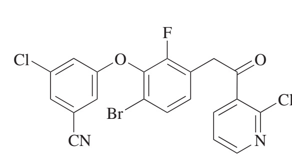
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20-22} 	DMSO, H_2O, 150°, 3.5 h	 m n o: 6 1 4 (80); 7 1 4 (75); 8 2 3 (78)	1261
C_{20} 	Collidine, LiI, reflux, 14 h	 (63)	1262
	DMSO, H_2O, NaCl, 125°, 20 h	 Config.: (*R*) (78); (*S*) (86)	1263
	DMSO, H_2O, LiCl, 160°, 24 h	 m n: 1 3 (83); 3 1 (91)	1264, 1265
	DMSO, H_2O, NaCl, 165°, 10 h	 (58)	699
	DMSO, NaCN, 90°, 22 h	 (70)	1266
C_{21} 	DMSO, H_2O, NaCl, 160–170°, 6 h	 (40)	1267
	DMF, LiBr, 150–160°, 48 h	 (50)	1267
	DMSO, H_2O, NaCl, 120°, 10 h	 (33)[b]	1268
	DMSO, H_2O, NaCl, 150°, 0.5 h	 (85)	1269,1270

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

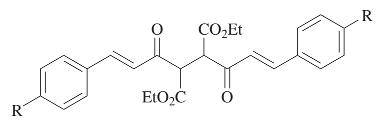
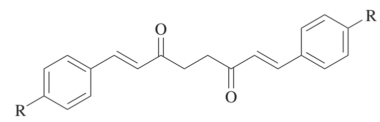
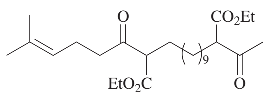
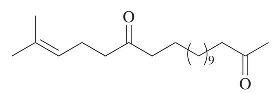
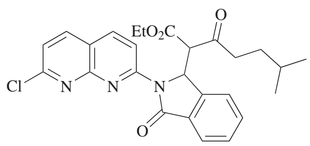
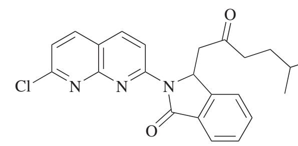
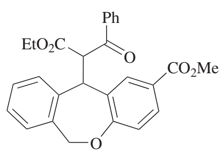
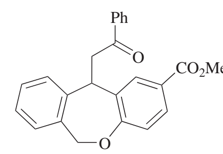
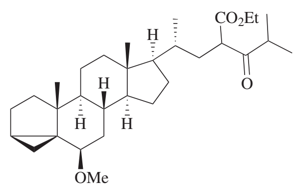
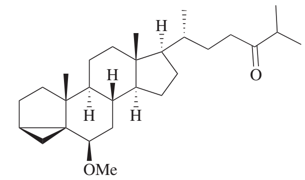
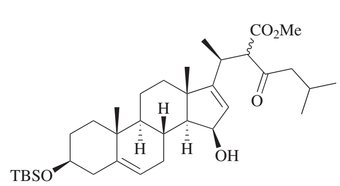
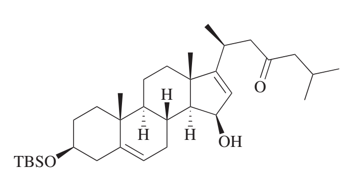
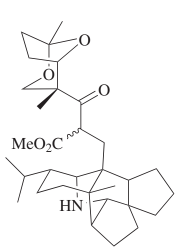
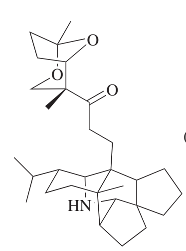
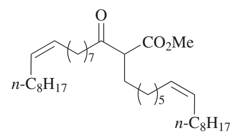
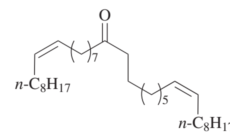
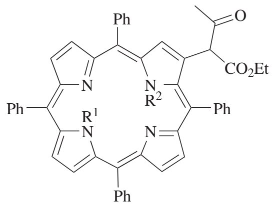
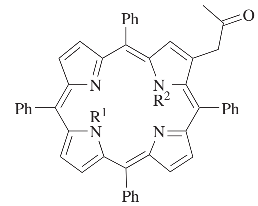
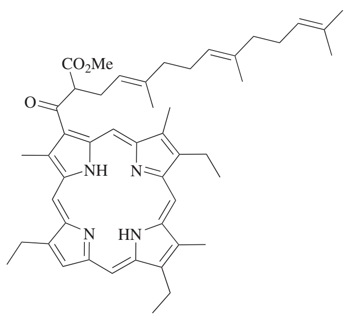
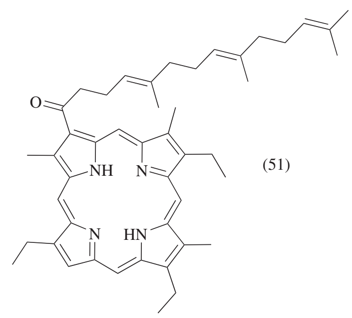
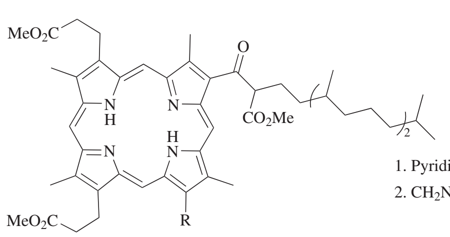
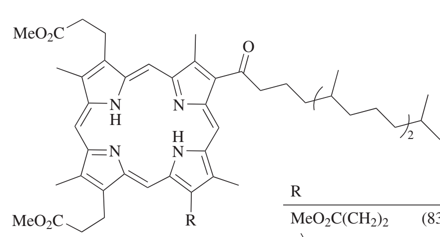
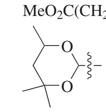
	β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}		H_2O, 10 atm, "heat", 4 h	 R: H (—); MeO (—)	1271
C_{23}		DMSO, H_2O, NaCl, 150°, 5 h	 (24)	1272
C_{24}		DMSO, H_2O, LiCl, reflux, 30 min	 (—)	1273
		DMSO, H_2O, NaCl, 150–160°, 8 h	 (42)	1274
C_{28}		Dioxane, H_2O, Al_2O_3, 100–105°, 96 h	 (98)	1275
		HMPA, H_2O, NaI, 180°, 15 min	 (97)	140, 1276
C_{31}		DMSO, H_2O, NaCN, 150°, 2 h	 (43)[b]	272

TABLE 9B. DEALKOXYCARBONYLATIONS OF ACYCLIC α-MONOSUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{36}			
	DMSO, H_2O, NaCl, 145°, 8 h	 (95)	1277
C_{48}			
	DMSO, H_2O, NaCl, 140°, 6 h	 R^1 R^2: H H (80); —Cu^{+2}— (83); —Ni^{+2}— (76)	1278
	Pyridine, 12-c-4, LiI•H_2O, reflux, 48 h	 (51)	1279
$C_{49–51}$			
	1. Pyridine, LiI, reflux, 45 h 2. CH_2N_2	 R: $MeO_2C(CH_2)_2$ (83);  (84)	1280

[a] The only structure proof was base titration.

[b] The yield includes that for the preparation of the substrate.

[c] The substrate was injected into the preheater of a gas chromatograph at 270º.

[d] This method gave a better yield than DMSO, H_2O, NaCl; NaCN, HMPA; KCl, DMF; or KI, DMSO.

[e] Decomposition was observed.

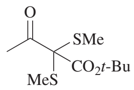
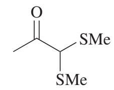
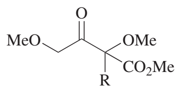
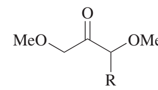
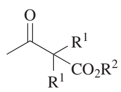
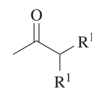
[f] This product was described in the text as the "acid cleavage product" and presumably should be the acid rather than the methyl ester. There was no description of the experiment.

[g] Product **II** was formed by isomerization of product **I**. The mechanism of this isomerization, which was observed with other 2-acyl-1,4-diketones, has not been determined.

[h] The BF_3•Et_2O was used in the preparation of the substrate in the same pot. The active reagents presumably were its hydrolysis products, hydrofluoric and boric acids.

[i] Other salts and DMSO or HMPA gave unsatisfactory results.

TABLE 9C. DEALKOXYCARBONYLATIONS OF ACYCLIC α,α-DISUBSTITUTED β-KETO ESTERS

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	DMSO, H_2O, 160°, 4 h	 (85)	323
C_{5-11} 	DMSO, H_2O, LiCl, 120–140°, 10 h	 R: Me (47); *n*-Pr (72); *i*-Pr (51); *n*-Bu (90); Bn (92)	1281
C_{6-8} 	See table.		

R^1	R^2	Solvent	Additive	Temp (°)	Time (h)		Refs.
Me	Me	H_2O	—	100	—	(—)	19
Me	Et	—	NaI	160–170	18	(6)	1142
Me	Et	—	NaI•2H_2O	150–160	2	(6)	1143
Me	Et	H_2O	—	250	12	(50)	1142, 19
Me	Et	$HO(CH_2)_2OH$	NaI	160–170	12	(32)	1142
Me	Et	PhOH	NaI	160–170	12	(7)	1142
Me	Et	—	CaI_2	130–150	2	(48)	1142
Me	Et	—	CaI_2•2H_2O	145–155	1.5	(78)	1143
Me	Et	$HO(CH_2)_2OH$	CaI_2	130–150	2	(65)	1142
Me	Et	PhOH	CaI_2	130–150	2	(56)	1142
Me	Et	DMSO	H_2O	reflux	4	(0)[a]	15
Et	Et	H_2O	—	250	12	(0)	1144

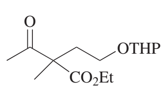
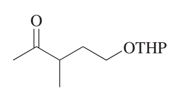
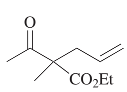
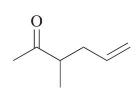
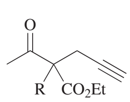
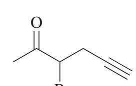
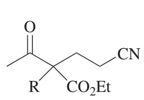
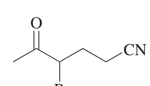
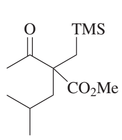
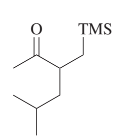
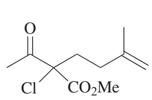
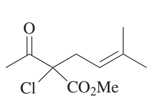
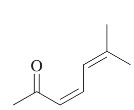
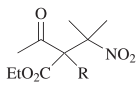
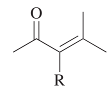
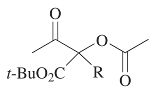
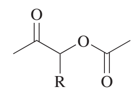
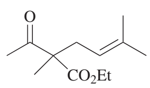
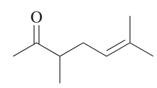
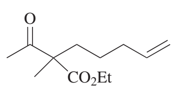
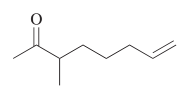
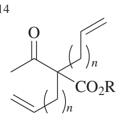
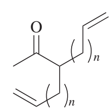
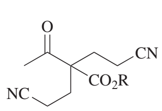
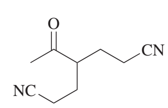
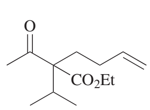
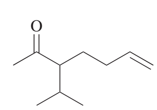
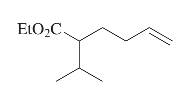
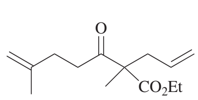
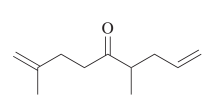
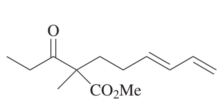
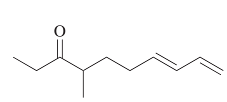
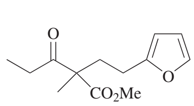
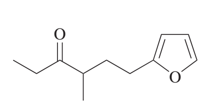
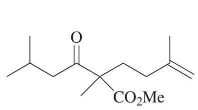
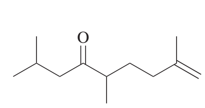
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	HMPA, NaCN, 110°, 4 h	 (56)	1282
C_8 	HMPA, NaCN, 110°, 4 h	 (43)	1282
C_{8-10} 	H_2O, Na_2CO_3, distill, 8 h	 R: Me (80); Et (80); CH≡CCH$_2$ (48)	1283
C_{8-9} 	H_2O, Na_2CO_3, "heat"	 R: Me (30); Et (29)	1178
C_9 	HMPA, NaCN, 90°, 6 h	 (68)	1284, 1285
 +  60:40	NMP, HCl, $(c\text{-}C_6H_{11})_2NEt$, LiCl, 150°, 3.5 h	 (76)	1286

TABLE 9C. DEALKOXYCARBONYLATIONS OF ACYCLIC α,α-DISUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-11} 	HMPA, NaBr, 130–140°, 4 h	 R: Et (51)[b]; *n*-Bu (60)	233
C_{9-14} 	DMSO, H_2O, LiCl, 145–160°, 5 h	 R: $Me_2C{=}CHCH_2$ (64); Bn (46); (*E*)-$Me_2C{=}CH(CH_2)_2C(Me){=}CHCH_2$ (82); (*Z*)-$Me_2C{=}CH(CH_2)_2C(Me){=}CHCH_2$ (69)	186
C_{10} 	DMSO, H_2O, NaCl, 170°, 5 h	 (14)	1287
	2,6-Lutidine, LiI•$2H_2O$, reflux, 20 h	 (89)	1288
C_{10-14} 	See table.		

n	R	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
1	Me	DMSO	H_2O, LiCl	160	3	(98)	1289
1	Et	DMF	LiCl	reflux	—	(90)	1290
3	Et	DMSO	H_2O, LiCl	149–152	20	(54)	1291

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	DMSO, H_2O, additive, reflux		18
C_{11} 	DMSO, NaCN, 160°, 4 h	 **I** (70) +  **II** (—) **I/II** = 4:1	197
C_{12} 	DMSO, H_2O, LiCl, 160°, overnight	 (64)	1292
	DMF, H_2O, LiCl, reflux, 18 h	 (70)	1293
	DMF, H_2O, LiCl, reflux, 18 h	 (80)	1293
C_{13} 	DMSO, H_2O, LiCl, 170°, 1.5 h	 (89)	1294

R	Additive	Time (h)	
Et	—	72	(8)
Et	LiCl	5	(59)
t-Bu	—	3	(60)
t-Bu	LiCl	5	(90)

TABLE 9C. DEALKOXYCARBONYLATIONS OF ACYCLIC α,α-DISUBSTITUTED β-KETO ESTERS (*Continued*)

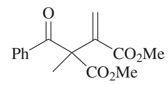
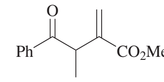
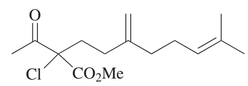
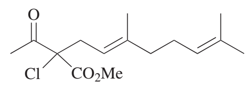
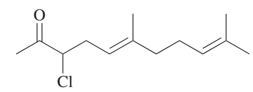
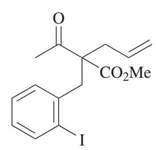
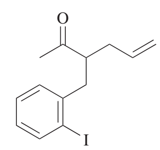
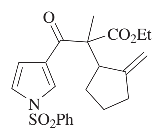
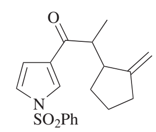
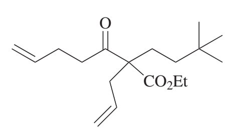
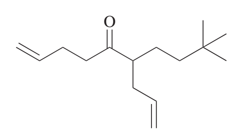
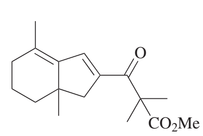
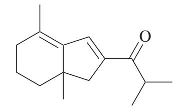
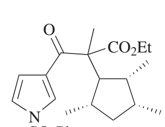
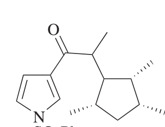
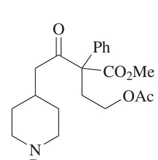
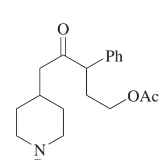
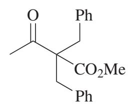
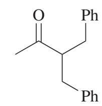
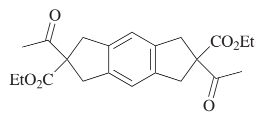
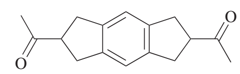
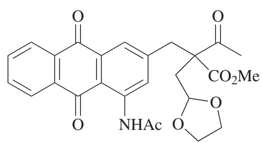
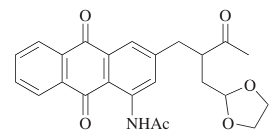
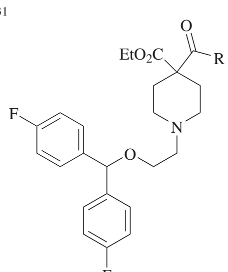
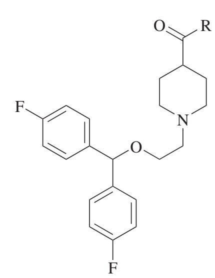
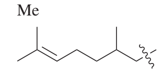
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	DMSO, H_2O, $MgCl_2$, 150°	 "low yield"	1295
C_{14}  I +  II **I/II** = 55:45	1. NMP, HCl (gas) 2. 2,6-Lutidine, LiCl, 90°, 1 h	 (100) 85% pure	1296, 1286
	DMSO, H_2O, LiCl, 150°, 3 h	 (77)	753
	HMPA, H_2O, LiCl, 130–135°, 14 h	 (70)	1233
C_{16} 	Collidine, LiI, 180°, 8 h	 (22)	1297
	*m*-Xylene, DABCO, 120°, 3 d	 (56)	1298
	HMPA, H_2O, LiCl, 130°, 24 h	 (70)	1299
C_{17} 	DMSO, H_2O, LiCl, 160°, 3 h	 (36)	1300

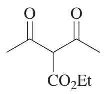
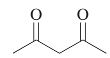
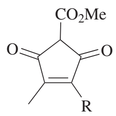
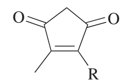
TABLE 9C. DEALKOXYCARBONYLATIONS OF ACYCLIC α,α-DISUBSTITUTED β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}			
	DMF, 4-$H_2NC_6H_4SH$, Cs_2CO_3, 85°, 3 h	 (100)	304
	DMSO, H_2O, NaCl	 (—)	1510
C_{21}			
	DMSO, LiCl	 (80)	1301
C_{23-31}			
	DMSO, H_2O, LiCl, reflux, 1 h	 R: Me (40) R:  (71)	1707

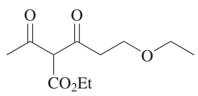
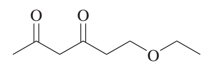
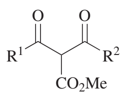
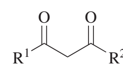
[a] Starting material was recovered in 90% yield.

[b] The yield includes that of the preparation of the substrate.

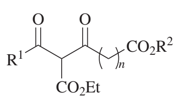
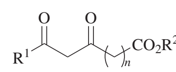
TABLE 10. DEALKOXYCARBONYLATIONS OF α-ACYL β-KETO ESTERS

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	B_2O_3, HOAc, reflux, 7.5 h	 (75)	1323
C_{7-12} 	DMSO, H_2O, NaCl, reflux, 1 h		1302

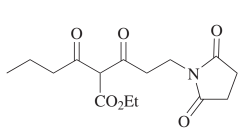
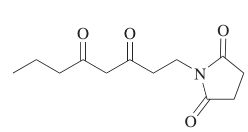
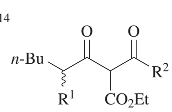
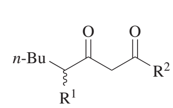
R	
MeO	(85)
n-Pr	(90)
n-Bu	(90)
n-C_5H_{11}	(90)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	H_2O, 115°, 40 min	 (31)	1303
C_{8-11} 	H_2O, 140–150°	 (—)	1304

R^1	R^2
Me	*n*-Pr
Me	*i*-Bu
Me	*n*-C_5H_{11}
n-Pr	*i*-Bu

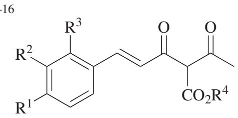
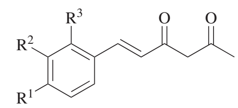
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-14} 	See table.		

n	R^1	R^2	Solvent	Additives	Temp (°)	Time (h)		Refs.
2	Me	Et	H_2O (1 eq)	—	150	—	(65–70)	1006
2	Et	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
2	*n*-Pr	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
2	$EtO_2C(CH_2)_2$	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
2	$EtO_2C(CH_2)_3$	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
2	$EtO_2C(CH_2)_4$	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
3	Me	Et	H_2O (1 eq)	—	150	—	(65–70)	1006
3	Me	Me	DMSO	H_2O, NaCl	reflux	8	(—)	1306
3	Et	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
3	*n*-Pr	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
3	$EtO_2C(CH_2)_3$	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
3	*n*-C_5H_{11}	Me	DMSO	H_2O, NaCl	reflux	8	(70)[a]	1306, 1307
3	$EtO_2C(CH_2)_4$	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
4	Me	Et	H_2O (1 eq)	—	150	—	(65–70)	1006
4	Et	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
4	*n*-Pr	Et	H_2O (1 eq)	—	150	—	(60–65)	1305
4	$EtO_2C(CH_2)_4$	Et	H_2O (1 eq)	—	150	—	(60–65)	1305

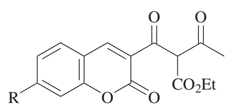
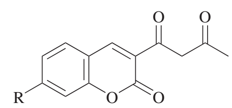
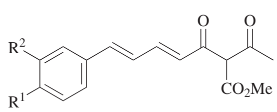
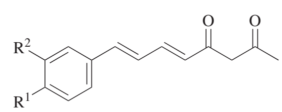
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	Pyridine, H_2O, reflux, 16 h	 (43)	1308
C_{10-14} 	DMSO, H_2O, NaCl, reflux, 12 h		1309

R^1	R^2	Config.		er
H	Me	(*R*,*S*)	(62)	—
Et	Me	(*R*,*S*)	(62)	—
Et	Me	(*R*)[b]	(99)	73.0:27.0
Et	*n*-Pr	(*R*,*S*)	(15)	—

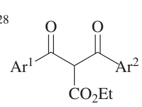
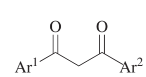
TABLE 10. DEALKOXYCARBONYLATIONS OF α-ACYL β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-16} 	See table.		

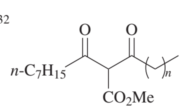
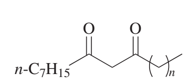
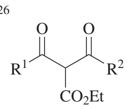
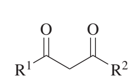
R^1	R^2	R^3	R^4	Solvent	Additives	Temp	Time (h)		Refs.
H	H	H	Et	H_2O	—	reflux	4	(40)	1310,1229
H	MeO	H	Et	H_2O	—	autoclave	—	(—)	1311
MeO	H	H	Me	H_2O	—	130°	6	(—)	1312
MeO	H	H	Me	DMSO	H_2O, NaCl	160–170°	4	(54)	163
O_2N	H	H	Et	H_2O	—	autoclave	3	(—)	1313
–OCH_2O–		H	Et	H_2O	—	autoclave	—	(—)	1311
AcO	H	AcO	Et	H_2O	—	autoclave	—	(—)	1311
i-Pr	H	H	Et	H_2O	—	autoclave	3	(—)	1311

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	H_2O, 3 atm, "heat"	 R: H (—); AcO (—)	1314; 1315
C_{15} 	H_2O		

R^1	R^2	Temp	Time (h)		Refs.
H	H	130°	6	"good"	1316, 1317
–OCH_2O–		autoclave	3	(—)	1318

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16-28} 	DMSO, H_2O, NaCl, 140°		1319

Ar^1	Ar^2	
Ph	4-$MeOC_6H_4$	(77)
Ph	2-naphthyl	(93)
Ph	4-(4-$MeOC_6H_4$)C_6H_4	(57)
2-naphthyl	2-naphthyl	(77)
4-PhC_6H_4	2-naphthyl	(50)
4-PhC_6H_4	4-PhC_6H_4	(83)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18-32} 	DMSO, H_2O, "heat"	 *n*: 6 (82); 20 (98)	1320
C_{20-26} 	DMSO, H_2O, NaCl, reflux, 8 h	 (40–60)	1321

R^1	R^2
n-Pr	*n*-$C_{13}H_{27}$
n-Pr	*n*-$C_{15}H_{31}$
n-Pr	*n*-$C_{17}H_{35}$
n-Pr	*n*-$C_{19}H_{39}$
n-C_5H_{11}	*n*-$C_{13}H_{27}$
n-C_5H_{11}	*n*-$C_{15}H_{31}$
n-C_5H_{11}	*n*-$C_{17}H_{35}$
Ph	*n*-$C_{13}H_{27}$
Ph	*n*-$C_{15}H_{31}$
n-C_9H_{19}	*n*-$C_{12}H_{25}$
n-C_9H_{19}	*n*-$C_{13}H_{27}$

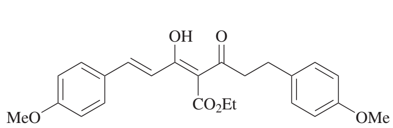
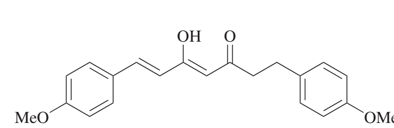
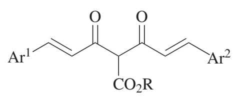
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	DMSO, H_2O, NaCl, 130–140°, 6 h	 (79)	163

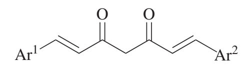
TABLE 10. DEALKOXYCARBONYLATIONS OF α-ACYL β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{20}



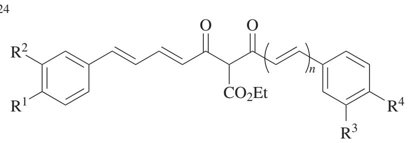
H_2O



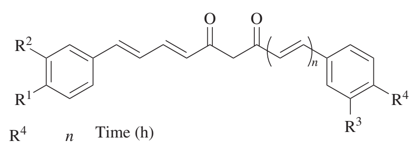
(—)

Ar[1]	Ar[2]	R	Temp	Time (h)	Refs.
Ph	Ph	Me	120–130°	6	1253
2-$AcOC_6H_4$	2-$AcOC_6H_4$	Et	autoclave (3 atm)	3	1322
2-$O_2NC_6H_4$	Ph	Et	autoclave (3.5 atm)	3	1313
2-$O_2NC_6H_4$	2-$O_2NC_6H_4$	Et	autoclave (5 atm)	3	1313
3-$O_2NC_6H_4$	3-$O_2NC_6H_4$	Et	autoclave (8 atm)	3	1313
4-$O_2NC_6H_4$	Ph	Et	autoclave (5 atm)	3	1313
4-$O_2NC_6H_4$	4-$O_2NC_6H_4$	Et	autoclave (7.5 atm)	5	1313

$C_{22–24}$



H_2O, autoclave (3 atm)



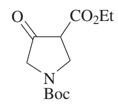
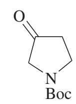
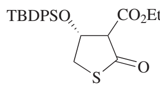
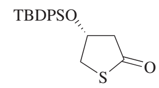
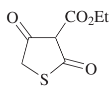
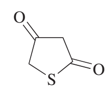
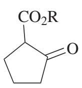
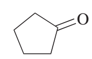
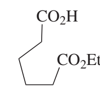
(—) 1317

R[1]	R[2]	R[3]	R[4]	*n*	Time (h)
H	H	MeO	AcO	1	4
–OCH_2O–		H	H	1	—
H	H	H	H	2	3

[a] The yield includes that of the preparation of the substrate.

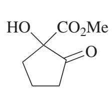
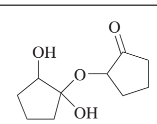
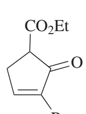
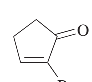
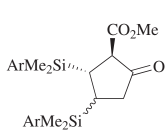
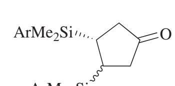
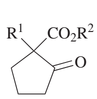
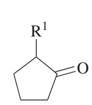
[b] The er of the starting material was not reported.

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	DMSO, H_2O, 120–130°, 4 h	 (70)	1324
	DMSO, H_2O, NaCl, 170°, 2 h	 (—)	1325
	H_2O, reflux, 2 h	 (55)	1326
C_6 	See table.	 **I** or  **II**	

R	Solvent	Additive	Temp	Time (h)	**I**	**II**	Refs.
Me	—	—	200°	0.5	(100)	(0)	1154
Me	dioxane	H_2O, Al_2O_3	reflux	2	(70)	(0)	310
Me	*o*-xylene	DABCO	reflux	4	(>96)	(0)	297
Et	dioxane	H_2O, Al_2O_3	reflux	2	(70)	(0)	310
Et	*o*-xylene	DABCO	reflux	4	(>96)	(0)	297
Et	DMSO	H_2O	120–142°	—	(75–80)	(0)	116
Et	EtOH, PhH	KOH, 18-c-6	rt; then reflux	2; 24	trace	(50)	330
n-Bu	*o*-xylene	DABCO	reflux	4	(>96)	(0)	297

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	MeCN, H_2O, MgI_2, 81°, 2 h	 (42)	1327
$C_{6–12}$ 	DMSO, H_2O, LiCl, 190°, 2 h	 R: H (87); Me (73); EtC≡CCH_2 (71); 4-ClC_6H_4 (87)	1328
C_6  Ar = 4-MeC_6H_4	DMSO, H_2O, NaCl, 130–150°, 3 h	 Config.: *cis* (86); *trans* (78)	261, 1329
$C_{7–14}$ 	See table.		

R^1	R^2	Solvent	Additive(s)	Temp (º)	Time (h)		Refs.
Me	Me	DMSO	H_2O, LiCl	160	8	(40)	1330
n-Pr	Me	DMSO	NaCN	160	3	(83)	1331
t-BuO$(CH_2)_3$	Me	DMF	H_2O, LiI	reflux	16	(75)	1332
$BnO(CH_2)_3$	Me	DMSO	LiCl	reflux	3.5	(81)	1333

$PhS(CH_2)_3$	Me	DMSO	NaCN	160	3	(87)	1334
n-Bu	Me	dioxane	H_2O, Al_2O_3	reflux	>200	(—)	310
2,5-$(MeO)_2C_6H_3S(CH_2)_4$	Me	2,4,6-collidine	$LiI{\bullet}2H_2O$	reflux	19	(81)	1335
2-furyl	Me	NMP	H_2O, HOAc, LiCl	reflux	1	(48)	237
n-C_5H_{11}	Me	DMSO	H_2O, NaCl	180	4	(35)	1336
3,4-$(OCH_2O)C_6H_3$	Et	DMSO	H_2O, LiCl	—	—	(0)	309
3,4-$(MeO)_2C_6H_3$	Et	DMSO	H_2O, LiCl	—	—	(0)	309
Bn	Me	2,4,6-collidine	$LiI{\bullet}2H_2O$	reflux	19	(72–76)	286
Bn	Me	HMPA	LiCl	75	24	(90)	22
Bn	Me	HMPA	NaCN	75	1	(80)[a]	22
$Ph(CH_2)_2$	Me	DMF	LiCl	reflux	10	(90)	1337

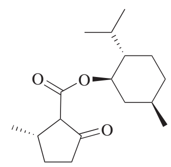
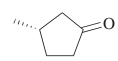
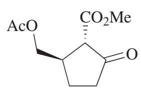
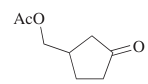
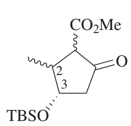
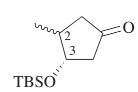
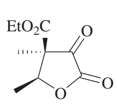
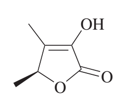
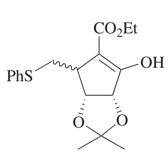
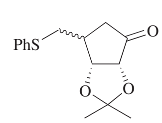
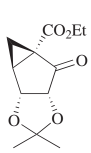
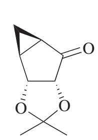
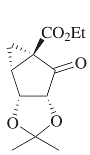
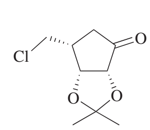
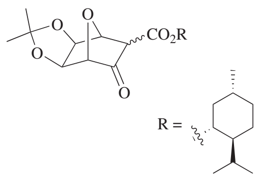
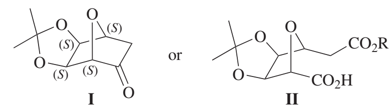
C_7 	DMSO, H_2O, NaCl, 165°, 2 h	 (—) "high er"	102
	DMSO, H_2O, NaCl, 160°, 3 h	 (95)	1338

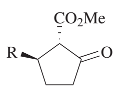
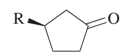
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	PhMe, H_2O, DMAP, 90°	 Config.: (2*R**,3*S**) (66); (2*S**,3*S**) (62)	1339, 1340
	DMSO, H_2O, LiCl, 125°, 12 h	 (80) 96.0:4.0 er	1341
	DMSO, H_2O, NaCl, reflux, 5 h	 Config.: α (78); β (76)	251, 1342
	DMSO, H_2O, NaCl, reflux, 5 h	 (18)	251
	DMSO, H_2O, NaCl, reflux, 5 h	 (23)	251

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	See table.		100

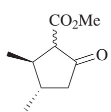
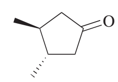
Solvent	Additive(s)	Temp (°)	Time (h)	I	II
DMSO	H_2O, $MgCl_2$	160	—	(0)	(0)
DMF	$LiI•2H_2O$	130	2.5	(41)	(0)
PhMe	DMAP, H_2O	reflux	—	(0)	(—)

$C_{8–12}$

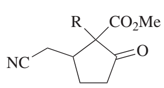
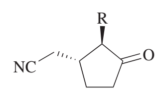
β-Keto Ester	Conditions	Product	Refs.
	DMSO, additive, 120°		

R	Additive	Time (h)		er	Refs.
CH_2=CH	DABCO	1	(88)	>97.5:2.5	105
t-Bu	DABCO	1	(89)	94.5:5.5	105
Ph	H_2O	13	(91)	83.5:16.5	104
Ph	DABCO	1	(76)	97.5:2.5	105

C_8

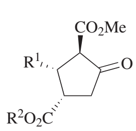
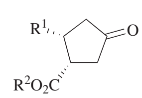
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, 120–148°, 5 h	 (65)	1343

$C_{8–13}$

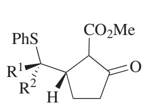
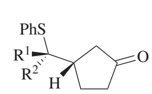
β-Keto Ester	Conditions	Product	Refs.
	DMSO, LiI		1344

R	Temp (°)	Time (h)	
H	—	—	(76)
EtC≡CCH_2	130	3	(85)

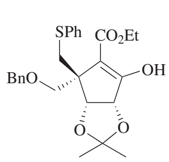
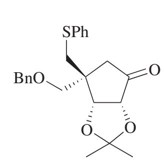
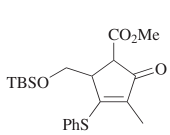
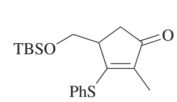
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{8–16}$ 	Diglyme, HOAc, NaI, reflux, 30 min		1345

R^1	R^2	
Me	Me	(85)
t-Bu	Me	(85)
$MeO_2C(CH_2)_3$	Me	(88)
Ph	Et	(98)
$EtO_2C(CH_2)_6$	Me	(75)
n-C_8H_{17}	Me	(79)
$EtO_2C(CH_2)_7$	Me	(89)
$Ph(CH_2)_3$	Me	(85)

β-Keto Ester	Conditions	Product	Refs.
$C_{8–10}$ 	DMSO, LiI		252

R^1	R^2	
H	Me	(98)
Me	H	(88)
(*E*)-MeCH=CH	H	(76)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	DMSO, H_2O, NaCl, reflux, 5 h	 (95)	251
	DMSO, H_2O, NaCl, 115°, 5 h	 (88)	1346

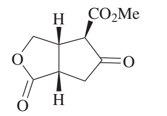
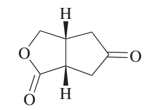
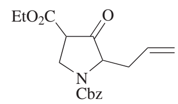
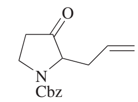
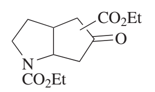
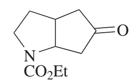
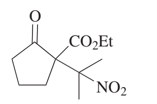
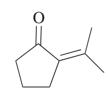
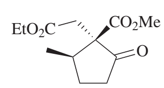
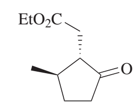
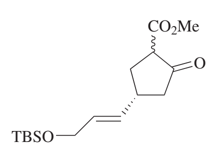
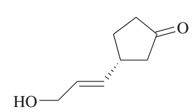
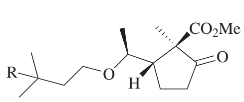
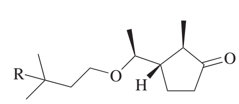
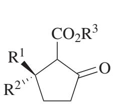
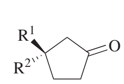
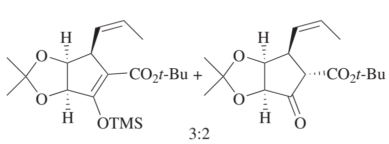
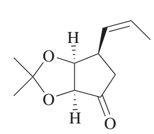
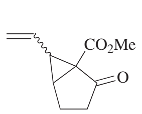
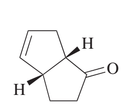
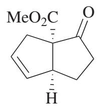
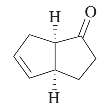
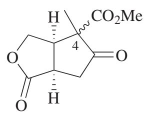
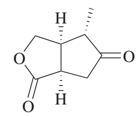
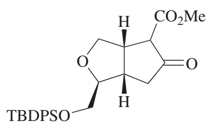
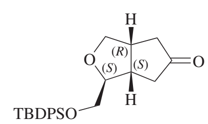
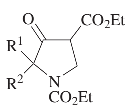
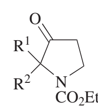
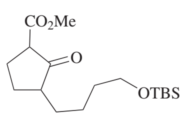
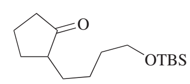
	DMF, H_2O, NaCl, 120°	 (96) >99.5:0.5 er	1347
	DMSO, NaCl, 125°, 4 h	 (64)	1348, 1349
	DMSO, H_2O, NaCl, 150°	 (51)[b]	1350
C_9 	HMPA, NaBr, 130–140°, 4 h	 (54)[b]	233
	DMF, LiI, reflux, 2 h	 (76)	1351

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

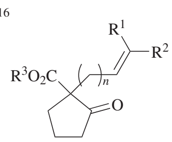
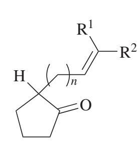
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, $MgCl_2$•$6H_2O$, 110°, 1 h	 (71)[b]	240, 1352
	HMPA, LiCl, 110°, 4 h	 R: H (62)[b]; HO (36)[b]	1353
$C_{9–11}$ 	DMSO, H_2O, NaCl, 150°, 3 h		190
C_9  3:2	"Wet" DMSO-d_6, 70°, 7.5 h	 (100)	95
	DMF, LiI, 110°, 3 h; then 135°, 4.5 h	 (71)	189

R^1	R^2	R^3		er
Me	Et	Me	(—)	88.5:11.5
Me	*i*-Pr	Me	(48)	83.0:17.0
Me	*n*-Bu	Me	(—)	82.5:17.5
n-Bu	Me	Et	(—)	91.0:9.0

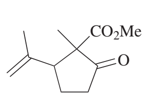
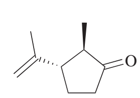
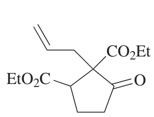
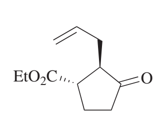
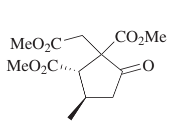
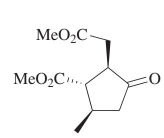
	DMF, LiI, 135°, 4.5 h	 (70)	1354
 (4*R*) or (4*S*)	DMF, H_2O, LiCl, reflux, 1 h	 (64)	57
	DMSO, H_2O, NaCl, 100°, 5.5 h	 (83)[b]	1355
C_{9-11} 	DMSO, H_2O, NaCl, 130°		1356
C_{10} 	Lutidine, LiI, heat	 (—)	1357

R^1	R^2	
H	*i*-PrCH(OH)	(91)
H	*n*-C_5H_{11}	(76)
H	*n*-C_5H_{11}CH(OH)	(77)
Me	*n*-C_5H_{11}	(83)

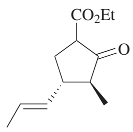
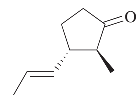
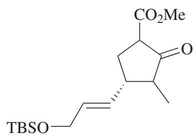
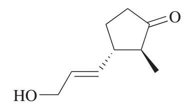
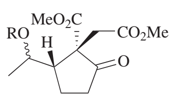
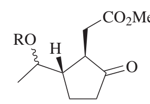
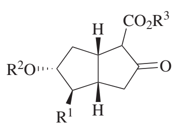
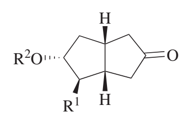
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-16} 	See table.		

n	R^1	R^2	R^3	Solvent	Additive	Temp (°)	Time (h)		
2	H	H	Et	DMSO	NaCN	150	1.5	(74)	1358
2	H	H	Et	2,6-lutidine	LiI	reflux	18	(—)	1359
3	H	H	Et	DMF	LiI	130–150	2	(—)	1360
4	H	H	Et	DMF	LiI	130–150	2	(—)	1360
1	H	CH_2=CH$(CH_2)_3$	Et	DMF	LiI•H_2O	reflux	6–8	(85)	1361
2	*n*-Pr	*n*-Pr	Me	2,4,6-collidine	LiI	reflux	—	(—)	1362

C_{10} 	HMPA, additive, 100°		
	DMF, LiI, reflux, 6 h	 (80)	1365
	DMF, LiI, reflux	 (—)	1366

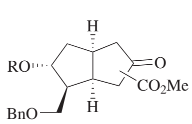
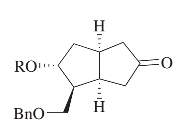
Additive	Time (h)		
$Me_4N^+AcO^-$	12	(72)	1363
LiCl	5	(63)	1364

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, NaCl, 130°, 3 h	 (100)	1367, 1368
	DMSO, $MgCl_2$•$6H_2O$, 160°, 12 h	 $(91)^b$	240
	HMPA, additive		
	See table.		

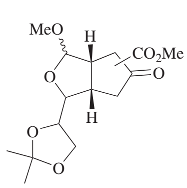
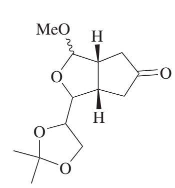
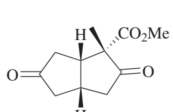
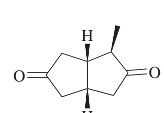
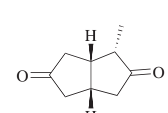
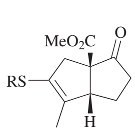
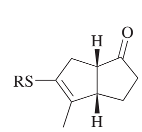
R	Config.	Additive	Temp (°)	Time (h)		Refs.
Me	(*S*)	NaI	100	3	(85)	1369
Bn	(*R*)	LiCl	130	4	(78)	1370

R^1	R^2	R^3	Solvent	Additives	Temp	Time (h)		Refs.
$TBSOCH_2$	H	Et	PhMe	H_2O, DABCO	110°	—	(—)	1371
$TrOCH_2$	H	Et	DMSO	H_2O, NaCl	—	—	(—)	1372
$BnOCH_2$	THP	Me^c	HMPA	H_2O	175°	0.25	(54)	1373, 1374
MeO_2C	H	Me	DMF	H_2O, NaCl	"heat"	1	(90)	1375

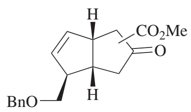
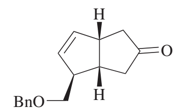
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	See table.		1373

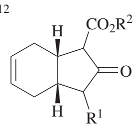
R	Solvent	Additive	Temp	Time (h)	
H	pyridine	LiI	"heat"	16	"good"
THP	HMPA	H_2O	175°	0.25	(37)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 120–125°, 4 h	 (72)	1376
	DMSO, H_2O, NaCl, reflux, 5 h	 +  (69) 2.7:1 dr	58
	HMPA, NaCN, 75°, 2 h		

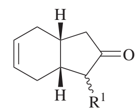
R		Refs.
Me	(82)	1377, 1378
Ph	(79)	1377

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 120°, 90 min	 (79)	1373

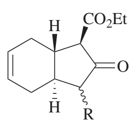
C_{10-12}



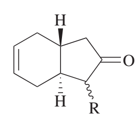
See table.



R^1	R^2	Solvent	Additive	Temp (º)	Time (h)		Refs.
H	Me	HMPA	H_2O	175	—	(96)	1379
H	Et	DMSO	H_2O	155	4.5	"high"	1380
H	Et	DMSO	H_2O	160	4	(95)	1381
Me	Et	DMSO	H_2O	160	4	(88)	1382
Et	Et	DMSO	H_2O	160	4	(50)	1382



DMSO, H_2O

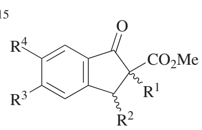


R	Temp (º)	Time (h)		Refs.
H	155	2.5	(92)	1383
H	160	4	(96)	1381
Me	160	4	(50)	1382
Et	160	4	(79)	1382

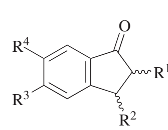
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{10-15}

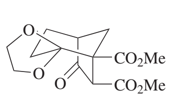
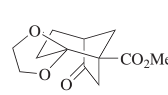
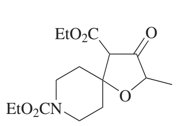
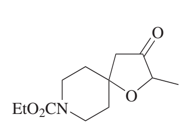


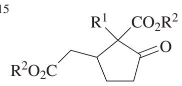
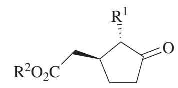
See table, reflux



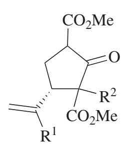
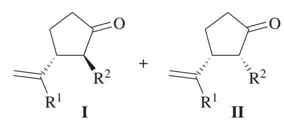
R^1	R^2	R^3	R^4	*trans/cis* R^1,R^2	Solvent	Additives	Time (h)		*trans/cis* R^1,R^2	Refs.
H	H	H	H	—	H_2O	Dowex-50	12	(82)	—	1595
(*S*)-EtCH(Me)	H	H	H	—	DMF	H_2O, LiI	3	(99)	—	1384
(*R*)-EtCH(Me)	H	H	H	—	DMF	H_2O, LiI	3	(100)	—	1384
(*S*)-(n-C_6H_{13})CH(Me)	H	H	H	—	DMF	H_2O, LiI	4	(87)	—	1384
2-furyl	H	MeO	MeO	—	DMF	H_2O, HOAc, LiCl	5	(75)	—	237, 1385
2-furyl	Me	MeO	MeO	—	NMP	H_2O, HOAc, LiCl	5	(63) R^3 = HO	—	237, 1385
2-furyl	Me	MeO	MeO	19:1	DMF	H_2O, HOAc, LiCl	—	(70)	9:1	1386

C_{10}

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyridine, LiI, reflux, 10 h	 (45)	1387
	DMF, H_2O, NaCl, 140–150°, 8 h	 (73)	1388

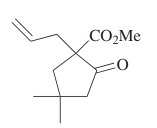
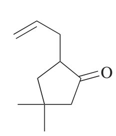
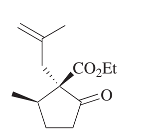
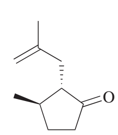
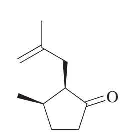
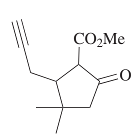
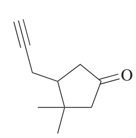
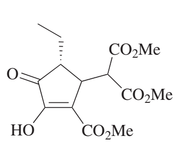
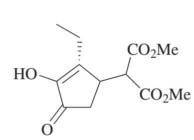
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-15} 	See table.		

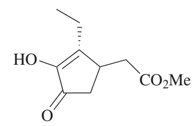
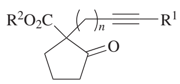
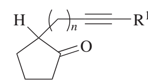
R^1	R^2	Solvent	Additive(s)	Temp (°)	Time (h)		
n-Pr	Et	DMSO	H_2O, NaCl	180	4	(43)	1336
n-Bu	Et	DMSO	H_2O, NaCl	180	4	(28)	1336
n-C_5H_{11}	Me	DMSO	H_2O, NaCl	170	18	(83)	1389, 1390
(*Z*)-EtCH=CHCH$_2$	Me	DMSO	H_2O, NaCl	176	4	(86)	1391, 1392, 1390
EtC≡CCH$_2$	Me	DMSO	H_2O, NaCl	180	3–4	(77)	1390
EtC≡CCH$_2$	Me	HMPA	NaCN	75	1	(84)	41
EtC≡CCH$_2$	Me	2,4,6-collidine	LiI•2H_2O	reflux	10	(71) R^2 = H	1393, 1394
HO(CH$_2$)$_2$C≡CCH$_2$	Me	2,4,6-collidine	LiI	40–80	6	(60)	1395
n-C_6H_{13}	Et	DMSO	H_2O, NaCl	180	4	(60)	1336
n-C_7H_{15}	Et	DMSO	H_2O, NaCl	180	4	(69)	1336

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl, 140°, 5 h	 I + II	

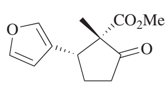
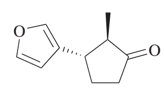
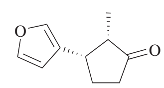
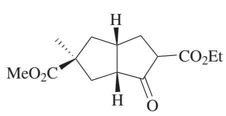
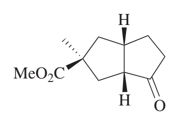
R^1	R^2	I + II	I/II	
H	Et	(40)	88:12	1396
Me	Me	(94)	92:8	1397

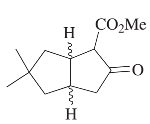
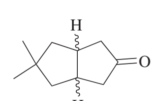
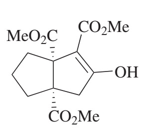
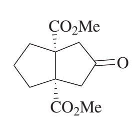
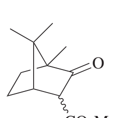
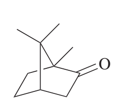
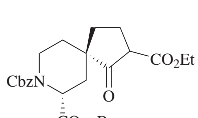
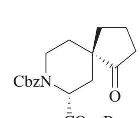
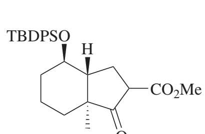
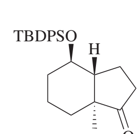
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	2,4,6-Collidine, LiI•2H_2O	 (79)	1398
	DMSO, NaCN, 140°, 36 h	 I +  II **I + II** (89), **I/II** = 9:1	1399
	DMSO, H_2O, LiCl, reflux, 2 h	 (—)	1400
	$MeCO_2H$, reflux, 26 h	 (80)	322

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	$EtCO_2H$, reflux, 72 h	 (60)	322
C_{11-12} 	See table.		

n	R^1	R^2	Solvent	Additive	Temp (°)	Time		Refs.
1	$AcO(CH_2)_2$	Me	DMSO	NaCN	160	2 h	(92)	1401
3	H	Me	DMF	LiI	150	50 min	(87)	1402, 356, 357
3	H	Et	DMF	LiI	—	—	(62)[b]	1403, 1360
3	TMS	Et	DMF	LiI	—	—	(65)[b]	1403
3	Me	Et	DMF	LiI	—	—	(60)[b]	1403
4	H	Et	DMF	LiI	130–150	2 h	(85)	1360

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	2,4,6-Collidine, $LiI\bullet 2H_2O$, 170–180°, 3 h	 **I** +  **II** **I + II** (89), **I/II** = 8:1	1404
	$MeO(CH_2)_2OMe$, H_2O, reflux, 48 h	 (63)[b]	1405

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl, 140°	 Config.: *cis* (—), *trans* (—)	1406
	DMSO, H_2O, NaCl, 140°, 2 h	 (92)	1407
	PhH, EtOH, KOH, 18-c-6, rt, 2 h; then reflux, 18 h	 (91)	330
	Dioxane, H_2O, 100°, 8 h	 (65)	1408
	DMF, $4\text{-}H_2NC_6H_4SH$, Cs_2CO_3, 85°, 12 h	 (34)	1409

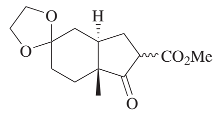
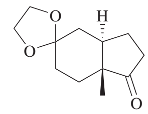
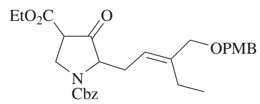
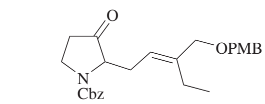
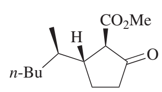
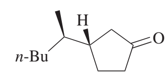
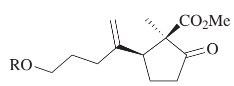
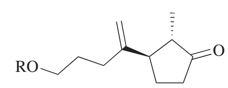
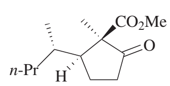
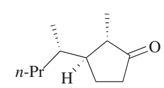
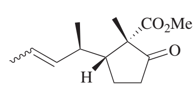
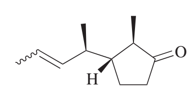
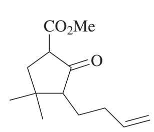
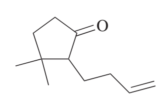
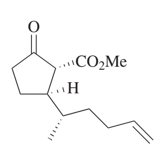
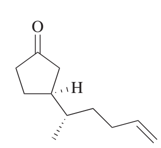
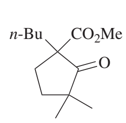
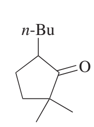
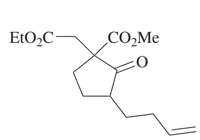
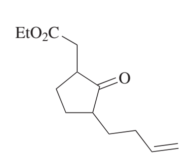
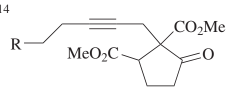
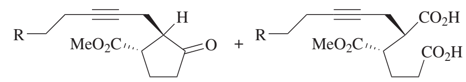
	DMSO, H_2O, NaCl, 160°, 4 h	 (77)	1410
	DMSO, NaCl	 (—)	1411
C_{12} 	DMSO, H_2O, NaCl, 160°, 5 h	 (66)	1412
	DMSO, DABCO, 120°	 R / Time (h) TBDPS 8 (62) Bn 9 (75)	1413 1414
	HMPA, LiCl, 100°, 3 h	 (63)	1415
	HMPA, NaCN, 75°, 7 h	 (51)	1416

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	DMF, LiI, reflux, 2 h	 (76)	1417
	DMSO, H_2O, NaCl	 (—)	1418
	2,4,6-Collidine, LiI•$2H_2O$	 (89)	1419
	HMPA, HOAc, LiCl, 110°, 17.5 h	 (82)	1420

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-14} 	See table.	 I + II	1421

R	Solvent	Additive(s)	Temp	Time (h)	I	II
H	2,4,6-collidine	LiI•$2H_2O$	reflux	10	(61)	(0)
$NCCH_2$	DMSO	H_2O, NaCl	155–160°	5	(53)	(39)
$NCCH_2$	2,4,6-collidine	LiI•$2H_2O$	reflux	—	(50)	(—)

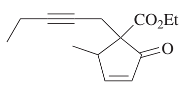
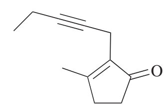
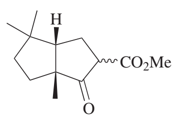
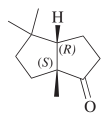
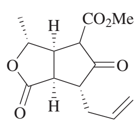
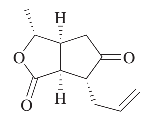
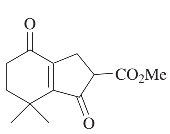
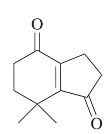
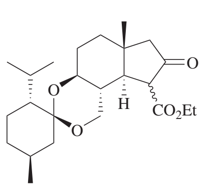
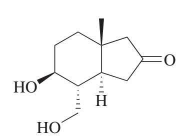
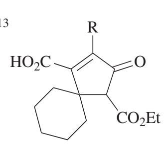
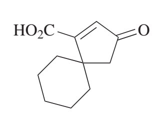
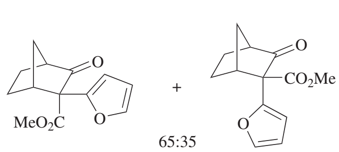
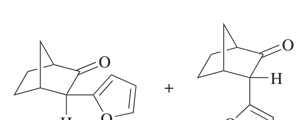
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	DMSO, H_2O, NaCl	 (32)	1422
	DMSO, H_2O, NaCl, 150–155°, 6 h	 (86)	1423
	DMF, H_2O, NaCl, 120°, 3 h	 (94)	1424

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	NMP, LiCl, 100°, 6 h	 (100)	1425
	DMSO, H_2O, LiCl, reflux, 30 min	 (78)	1426
C_{12-13} 	H_2O, 200°, "few" min	 "good yield" R: H, HO_2C, EtO_2C	1427
C_{12}  65:35	DMF, HOAc, H_2O, LiCl, reflux, 5 h	 I + II; **I + II** (84), **I/II** = 55:45	1386

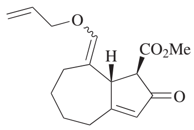
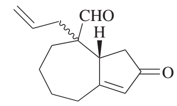
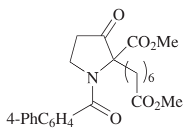
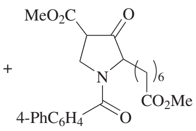
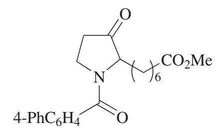
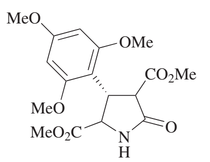
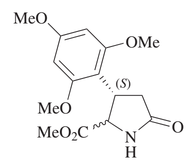
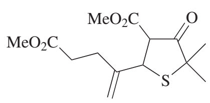
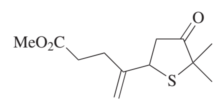
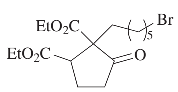
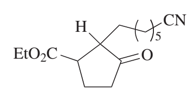
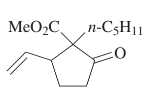
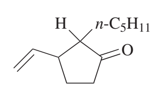
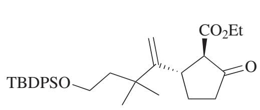
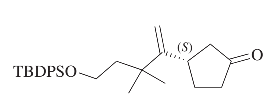
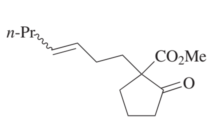
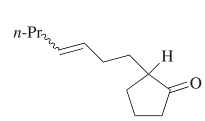
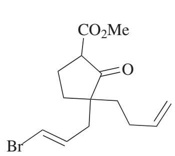
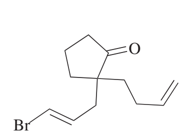
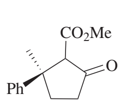
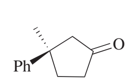
	PhCN, H_2O, reflux	 (73) 2:1 dr	1428
 + 	DMSO, H_2O, NaCl, 140°	 (65)	1429, 1430
	NMP, H_2O, NaCl, 170°, 5 h	 (44)	1431
	DMSO, H_2O, NaCl, 140–150°, 3 h	 (96)	1432
C_{13} 	DMSO, H_2O, NaCN, 115–120°; then 135–145°, 2 h	 (75)	1433

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	HMPA, NaI	 (88)	1434
	DMSO, DABCO, 120°, 6 h	 (88)	1435
	DMSO, H_2O, NaCN, 140°, 70 min	 Config. (*E*) (53); (*Z*) (—)	1436
	DMSO, H_2O, LiCl, 120°	 (86)	1437
	DMSO, H_2O, reflux, 1 d	 (64) >99.0:1.0 er	1438

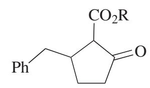
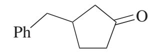
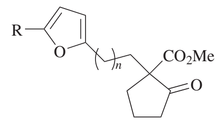
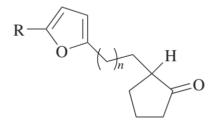
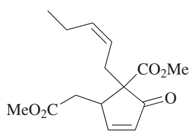
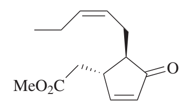
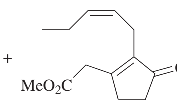
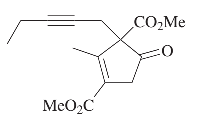
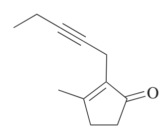
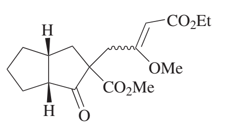
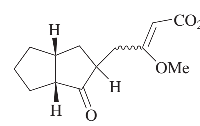
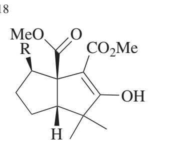
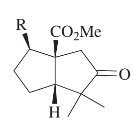
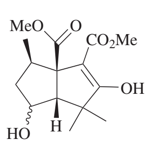
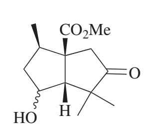
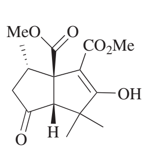
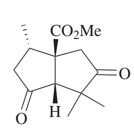
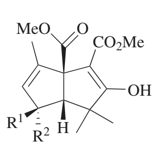
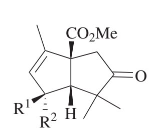
	PhMe, DMAP, phosphate buffer (pH 7), 90°, 6 h	 R: Me (70); n-Bu (71)	87
C_{13-14} 	DMF, H_2O, LiCl, reflux, 12–36 h	 n, R: 2, H (73); 2, Me (72); 3, H (72)	1439
C_{13} 	DMSO, H_2O, NaCl, 180°, 3–4 h	 **I** +  **II** **I + II** (46), **I/II** = 2:1	1391
	DMSO, H_2O, NaCl, 150°, 7.5 h	 (33)	1440
	2,4,6-Collidine, LiI	 (75)	1441

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-18} 	DMSO, H_2O, NaCl	 R, Temp (°), Time (h): Me, "heat", —, (74); NC, 94, 5, (69); MeO_2C, 120, 10, (74); Ph, 96, 6, (65)[b]	1443; 1442, 1443; 1444; 1442, 1443
C_{13} 	DMSO, H_2O, NaCl	 Config., Temp, Time (h): β, "heat", —, (62); mixture, 80°, 24, (68)	1445; 1446
	DMSO, H_2O, NaCl, 112°, 18 h	 (56)	1446
	DMSO, H_2O, NaCl, 80°	 R^1, R^2, Time (h): H, HO, 14, (99); =O, 11, (83)	1446

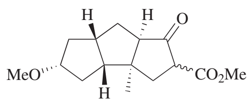
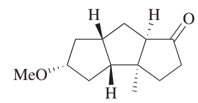
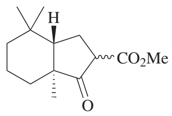
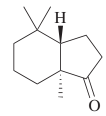
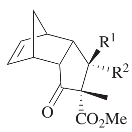
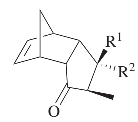
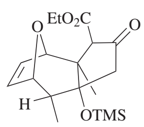
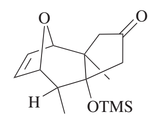
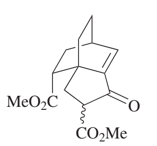
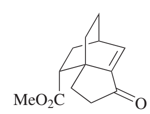
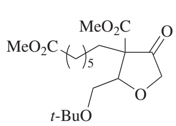
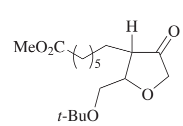
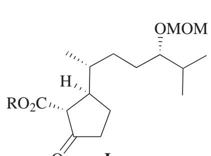
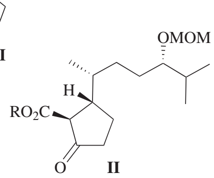
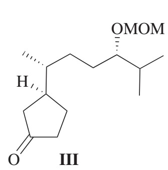
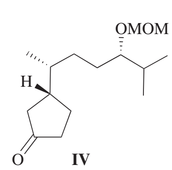
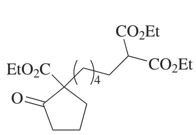
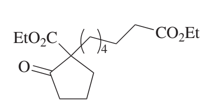
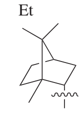
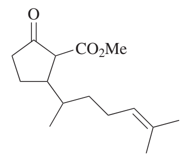
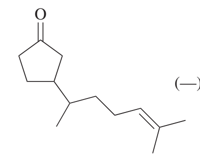
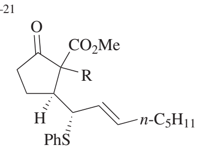
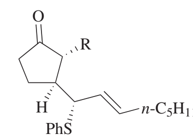
	DMSO, H_2O, LiCl, sealed tube, 180°, 10 h	 (82)	1447
	DMSO, H_2O, LiCl, 140°, 2 h	 (91)	1448, 1449
	DMF, LiI•$2H_2O$, reflux, 4 h	 R^1 / R^2: H, Me (60); Me, H (60)	1450
	DMSO, H_2O, NaCl	 (86)	1451
	DMSO, H_2O, NaCl, 110°, 16 h	 (72)	1452

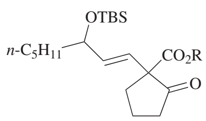
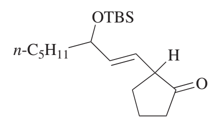
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	DMF, LiI	 (45)	1453
C_{14}			
 I +  II	DMSO, H_2O, LiCl, 3 h	 III +  IV	99
	DMSO, H_2O, NaCl, reflux; or DMF, LiI, "heat"; or collidine, *p*-cymene, "heat"	 (—)	86

R	I/II	Temp (°)	III + IV	III/IV
Et	65:35	120–130	(64)	71:29
	100:0	120–140	(68)	100:0

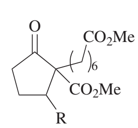
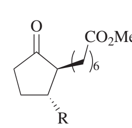
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl	 (—)	1418
C_{14-21} 	See table.		1454

R	Solvent	Additive	Temp (°)	Time (h)	
H	DMSO	LiI	—	—	(61)
$MeO_2C(CH_2)_6$	HMPA	LiCl	100	6	(92)

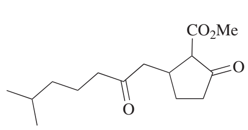
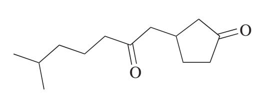
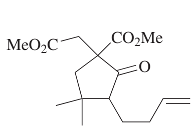
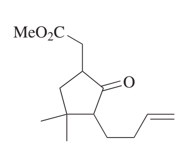
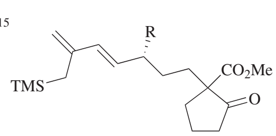
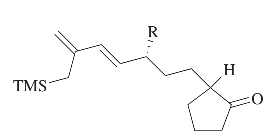
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	—		1455, 1354

R	
Me	(0)
Bn	(0)

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	See table.		

R	Solvent	Additive	Temp	Time		Refs.
$(MeO)_2CH$	HMPA	NaCN	70°	1 h	(90)	1456, 1457
$PhSCH_2$	DMF	LiI	reflux	—	(70)	1458

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, LiCl, 120°, 1.5 h	 (66)	1459
	2,6-Lutidine, $LiI•2H_2O$, reflux, 36 h	 (81)	1460
C_{14-15} 	DMSO, H_2O, KCN, reflux, 30 min		1461

R	
H	(66)
Me	(83)

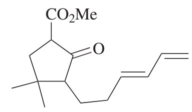
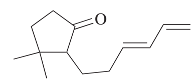
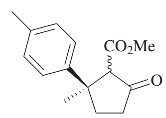
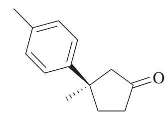
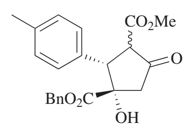
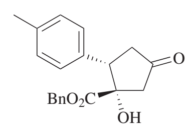
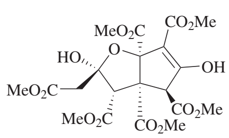
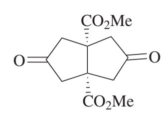
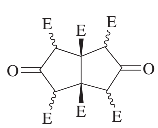
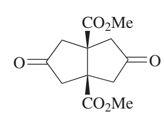
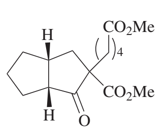
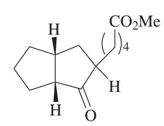
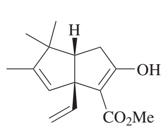
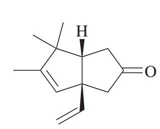
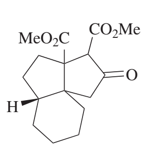
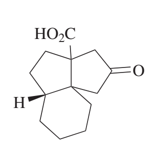
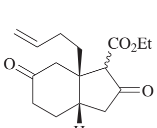
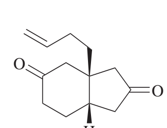
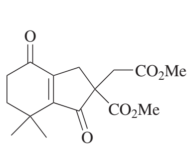
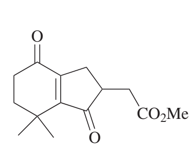
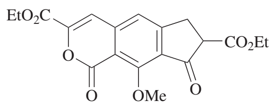
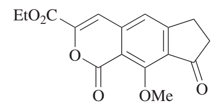
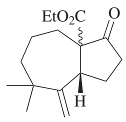
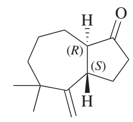
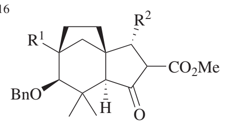
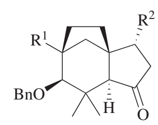
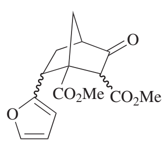
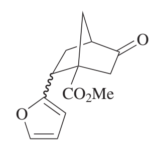
C_{14}		DMSO, H_2O, LiCl	 (—)	1462
		DMSO, H_2O, NaCl, 130–140°, 3.5 h	 (61)	1463
		DMSO, NaI, 100°, 3 h	 (89)	1464
		DMSO, H_2O, NaCl, 140°, 4 h	 (100)	1465
	 E = CO_2Me	DMSO, H_2O, NaCl, 130–140°, 4 h	 (—)	1407

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

	β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}		Collidine, LiI	 (50–60)	1466
		DMSO, H_2O, NaCl, 180°, 2 h	 (87)	325
		DMSO, H_2O, LiCl, 165–170°, 8 h	 (67)	260
		DMSO, H_2O, NaCl	 (45)	1467
		NMP, H_2O, LiCl, 120–125°, 6 h	 (70)	1468

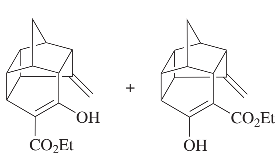
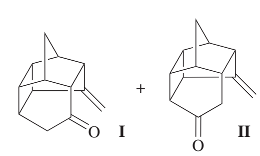
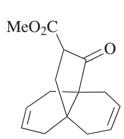
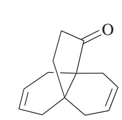
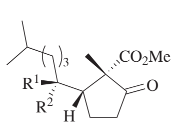
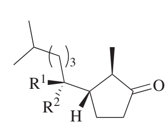
	Krapcho	 (92)	1469
	DMPU, LiCl, 130°, 74 h	 (13)	55
C_{14-16} 	See table.		

R^1	R^2	Solvent	Additive	Temp (°)	Time (h)		Refs.
H	H	DMSO	NaCl	150	8	(88)	1470
H	Me	*o*-xylene	DABCO	85	7	(84)	1470
MeO	H	PhMe	DABCO	95	4	(87)	1472, 1471
Me	Me	*o*-xylene	DABCO	85	7	(82)	1473

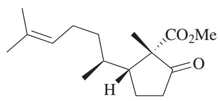
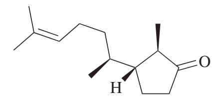
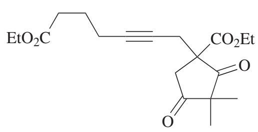
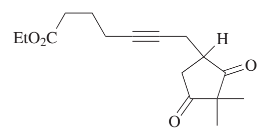
C_{14} 	Solvent, LiI		290

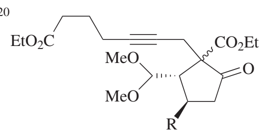
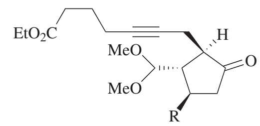
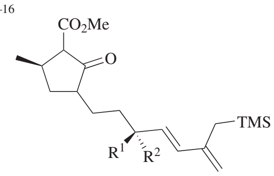
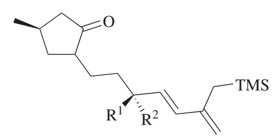
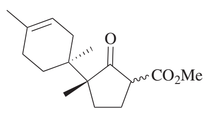
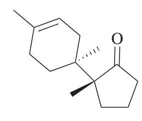
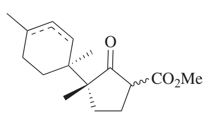
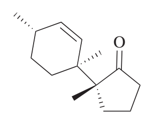
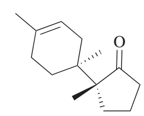
C-2 Config.	Solvent	Temp (°)	Time (h)	
α	pyridine	reflux	—	"good"
β	pyridine	reflux	48	(97)
β	collidine	140	4	(25)[d]

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	DMSO, H_2O, NaCl, 150°, 2 h	 **I** + **II** (92), **I**/**II** = 15:1	1474
	DMF, H_2O, NaCl	 (89)[b]	1475
C_{15} 	HMPA, NaCN, 75°		

R^1	R^2	Time (h)		Refs.
H	Me	5	(72)	1476, 1477
Me	H	3	(53)	1477

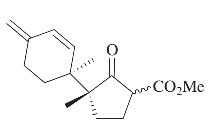
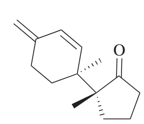
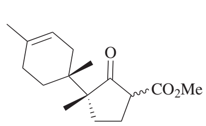
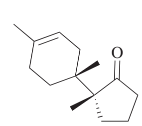
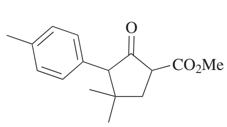
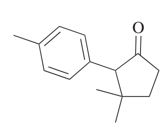
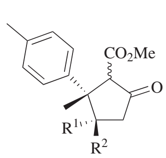
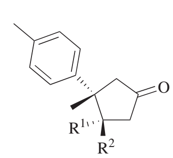
	HMPA, NaCN, 75–80°, 1 h	 (73)	1478
	DMF, LiI, reflux	 (76)	1479

C_{15-20} 	HMPA, NaCN, 75–80°		1457
C_{15-16} 	DMSO, H_2O, KCN, reflux, 30 min		1461
C_{15} 	2,4,6-Collidine, DBU, 180°, 3 h	 (78)	1480
	Xylene, DBU, reflux, 16 h	 I +  II **I + II** (98), **I/II** = 64:36	296

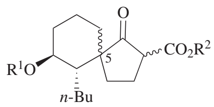
R	Time (h)	
Me	1.5	(94)
Ph	6	(99)

R^1	R^2	
H	H	(78)
H	Me	(74)
Me	H	(94)

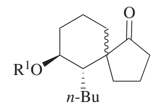
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

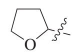
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	2,4,6-Collidine, DBU, 180–185°, 2.5 h	 (75)	296
	2,4,6-Collidine, DBU, 175–185°, 3 h	 (95) racemate	296
	DMSO, H_2O, NaCl, 170°, 30 h	 (88)	1481
	DMSO, NaI, 100°, 3 h		1464

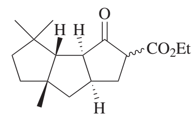
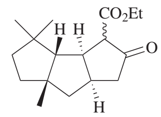
R^1	R^2	
BnO_2C	HO	(89)
HO	BnO_2C	(89)



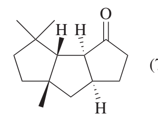
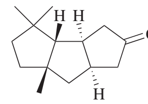
See table.

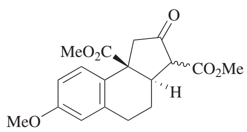


R^1	R^2	C-5 Config.	Solvent	Additive(s)	Temp	Time		Refs.
H	Me	(*S*)	xylene	DABCO	reflux	—	(67)	1482
	Et	(*R*)	DMSO	H_2O, LiCl, $NaHCO_3$	150°	3 h	(92)	1483

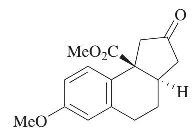
 + 

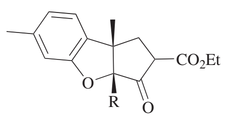
DMSO, H_2O, NaCl, 150°, 5 h

 (73)[b] +  (13)[b] 1484

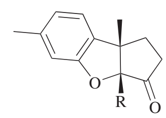


DMSO, H_2O, NaCl

 (40) 1485

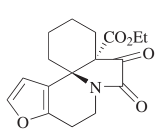
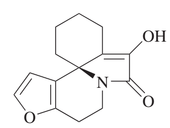
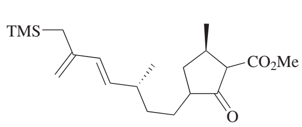
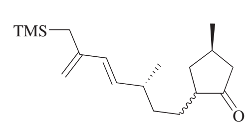
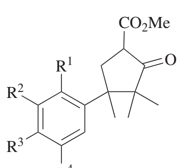
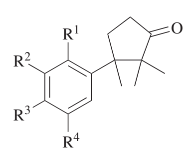
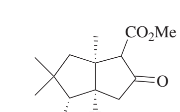
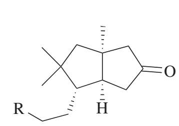


DMSO, H_2O, LiCl, 165–170°, 6 h



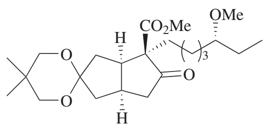
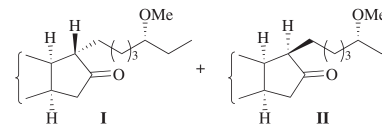
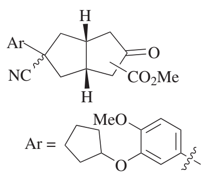
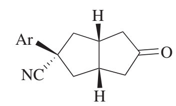
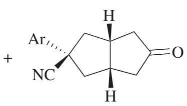
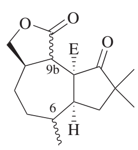
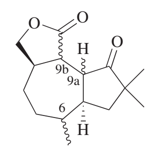
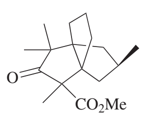
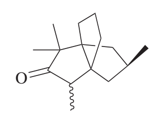
R		
Me	(81)	1486, 1487
$MeOCH_2$	(94)	

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	DMSO, $MgCl_2$, 160°, 3 h	 (83)	110
C_{16} 	DMSO, KCN, reflux	 (94)	1488
	DMSO, NaCl, 150–155°		
	DMSO, H_2O, LiCl		

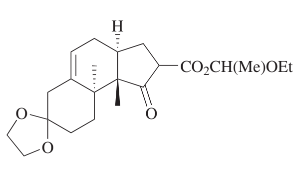
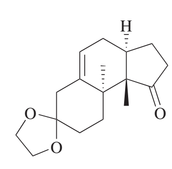
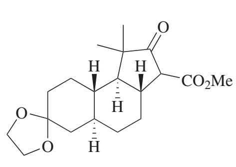
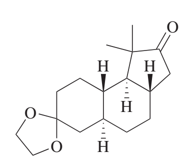
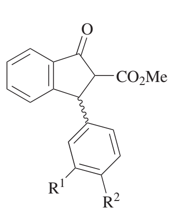
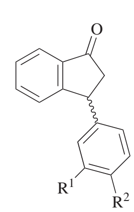
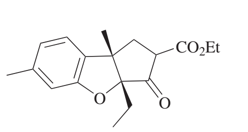
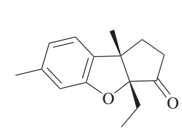
R^1	R^2	R^3	R^4	Temp (º)		Refs.
H	H	H	Me	155	(74)	1489
H	H	MeO	Me	155	(72)	1489
MeO	H	H	Me	150	(75)	1490
MeO	H	Me	MeO	150	(72)	1490
MeO	MeO	H	Me	155	(73)	1489

R	Temp (º)	Time		Refs.
CH_2=CH	145[e]	—	(96)	1491
TMSC≡C	140	15 min	(—)	1492

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	o-Xylene, DABCO, reflux, 16 h	 **I + II** (67), **I/II** = 3:1[f]	1493
	DMSO, H_2O, NaCl, 160°	 (48)[b] +  (22)[b]	1494
 E = CO_2Me	DMSO, H_2O, NaCl, 150°		56, 1495
	2,4,6-Collidine, LiI, reflux	 (95)	1496

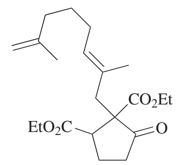
Relative Config.	Time (h)		C-9a Config.
6α,9bβ	6	(60)	β
6β,9bα	7.5	(36)	α

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

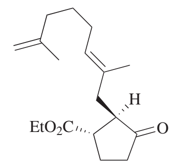
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	DMSO, H_2O, NaCl, 70°, 3 h	 (73)[b]	274
	DMSO, H_2O, LiCl, 170°, 1.25 h	 (92)	1497
	DMSO, H_2O, 120°, 30 min		1498
	DMSO, H_2O, LiCl, 160°	 (—)	1499

R^1	R^2	Config.		er
H	H	α	(93)	82.0:18.0
—OCH_2O—		β	(93)	81.5:18.5

C_{17}

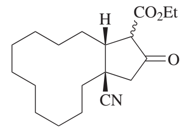


DMF, LiI, reflux, 5–6 h

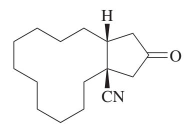


(70)

1365, 1500

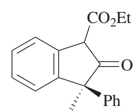


Diglyme, NaI, reflux, 1 h

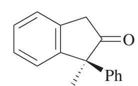


(97)

1501

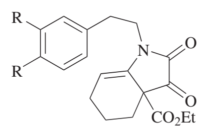


DMSO, H_2O, 120°, 30 min

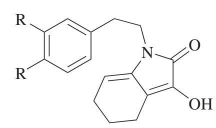


(97)

1502



DMSO, $MgCl_2$



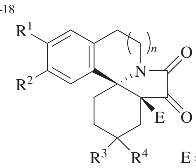
R	Temp (°)	Time (h)	
H	150	1	(51)
MeO	150–155	2	(55)

110, 109

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

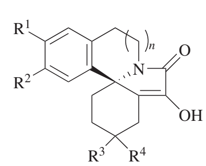
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.

$C_{17–18}$



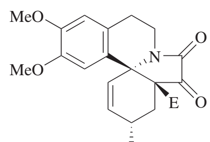
E = CO_2Et

See table.



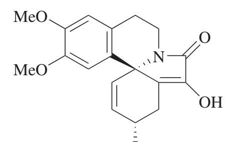
n	R^1	R^2	R^3	R^4	Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
1	H	H	H	H	HMPA	$MgCl_2$	160	3	(63)	110, 109
1	H	MeO	H	H	DMSO	$MgCl_2$	165	5	(62)	110
1	MeO	MeO	H	H	DMSO	H_2O, NaCl	170	24	(27)	110
1	MeO	MeO	H	H	DMSO	$MgCl_2$•$6H_2O$, EtSH	155–160	3	(63)	110
1	MeO	MeO	H	H	DMSO	$CaCl_2$•$2H_2O$, EtSH	150	5	(43)	110
1	MeO	MeO	H	H	HMPA	$MgCl_2$	150–155	2	(73)	110, 109
1	MeO	MeO	—O$(CH_2)_2$O—		HMPA	$MgCl_2$	145	2	(98)	110, 1503
2	—OCH_2O—		—O$(CH_2)_2$O—		DMSO	$MgCl_2$, Et_3CSH	"heat"	—	(91)	1504

C_{17}



E = CO_2Et

HMPA, $MgCl_2$, Et_3CSH, 145°, 1.5 h



(68)

1505

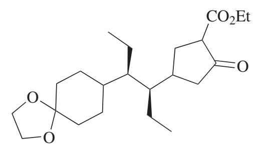
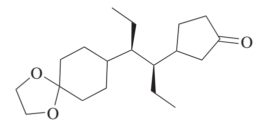
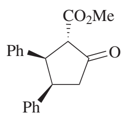
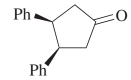
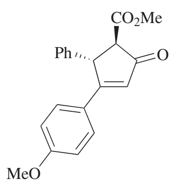
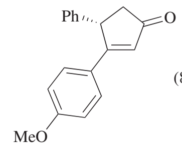
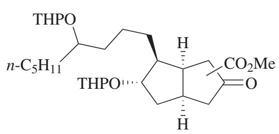
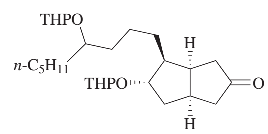
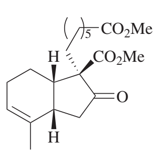
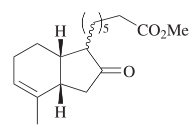
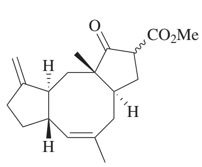
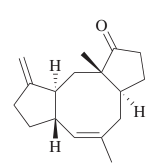
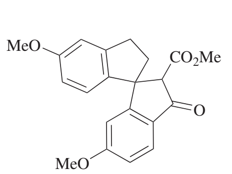
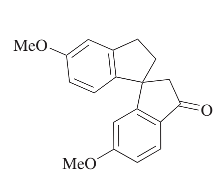
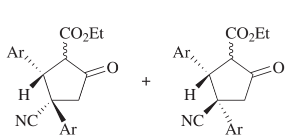
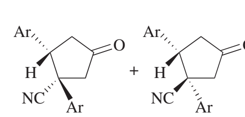
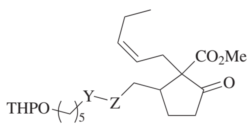
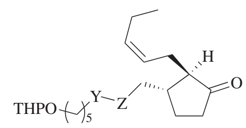
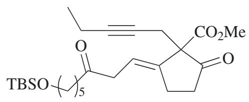
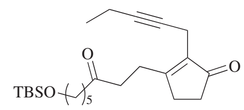
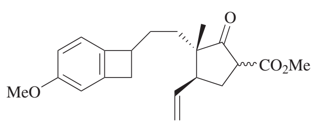
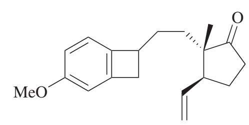
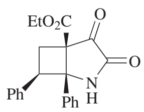
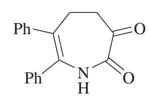
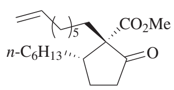
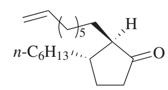
C_{18}		Pyridine, "heat", 5 h	 (—)	1506
		DMSO, H_2O, NaCl, 140°	 (—)	1406
		DMSO, H_2O, 110°, 12 h	 (87)	188
		DMF, $CaCl_2$, reflux, 2 h	 (80)	1507

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

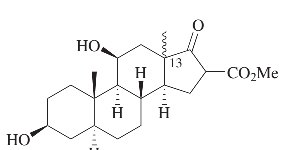
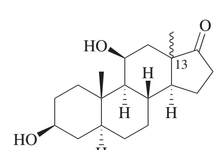
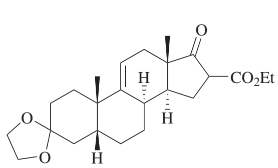
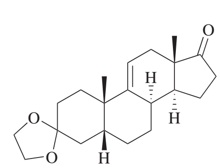
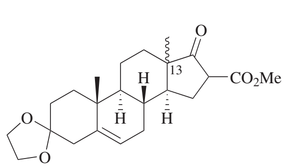
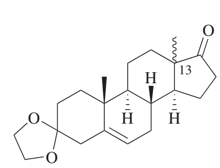
	β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}		1. Collidine, LiI•$2H_2O$, reflux, 11 h 2. CH_2N_2	 (74) *exo*/*endo* = 6:1	1508
		Collidine, LiI, 155°, 30 min	 (76)[b]	1509
		DMSO, H_2O, 150°, 1 h	 (100)	1511
C_{19}		Solvent, H_2O, NaCl, 120°, 1.5–2.5 h	 Ar / Solvent 2-$EtOC_6H_4$ / DMSO (90) 3,4-$(OCH_2O)C_6H_3$ / DMF (70)	1512

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	HMPA, NaCN, 75°		1513
	2,6-Lutidine, H_2O, LiI, 130°, 10 min	 (34)	1514
	DMSO, H_2O, NaCl, 165°, 45 min	 (69)	1515
	DMSO, $CaCl_2$, 150°, 20 min	 (31)	1516
C_{20} 	HMPA, LiCl, 100°, 5 h	 (51)	1517

Ref. 1513:

Y–Z	
CH_2CH_2	(75)
C≡C	(67)

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	Dioxane, H_2O		1518
	DMSO, H_2O, NaCl	 (—)	1519
	*p*-Cymene, reflux		1520

Ref. 1518:

C-13 Config.	Temp (°)	Time (min)	
α	200–210	35	(52)
β	220–222	41	(48)

Ref. 1520:

C-13 Config.	Time (h)	
α	1	(—)
β	2	(60)

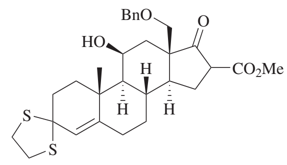
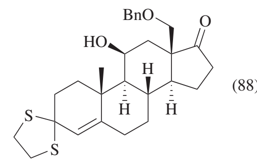
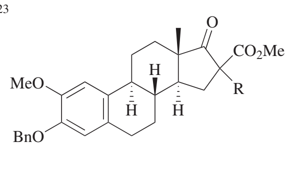
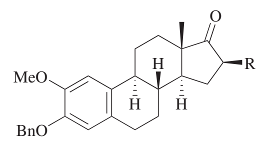
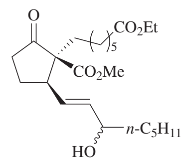
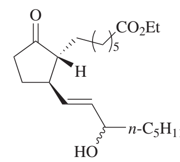
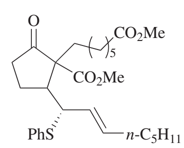
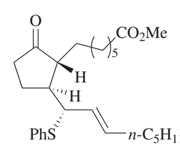
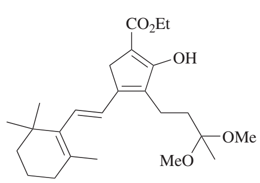
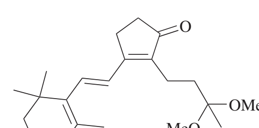
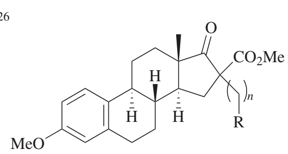
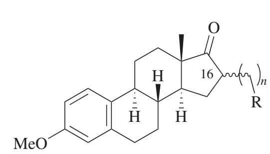
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyridine, NaI, reflux, 16 h	 (88)	1521
C_{20-23}			
	DMF, H_2O, LiCl, reflux, 24 h	 R: Me (44); allyl (66); crotyl (92)	1522
C_{21}			
 1:1 dr	HMPA, NaCN, 75–80°	 (87)	1457
	HMPA, LiCl, 100°, 6 h	 (92)	1454

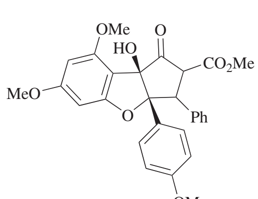
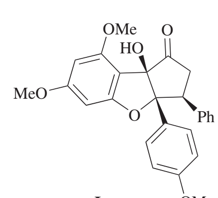
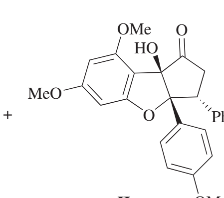
TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

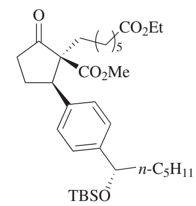
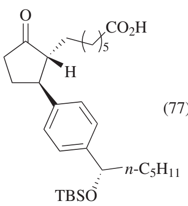
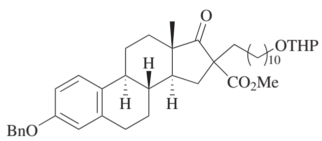
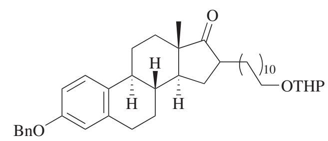
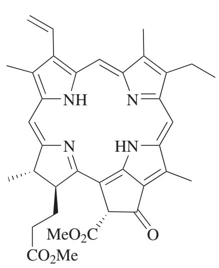
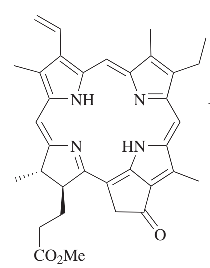
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	See table.		1523

Cond.	
DMSO, H_2O, salts, "heat"	(0)
MeOH, H_2O, KOH, reflux, 24 h	(45)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23-26}			
	DMF, H_2O, LiCl, reflux, 18 h		

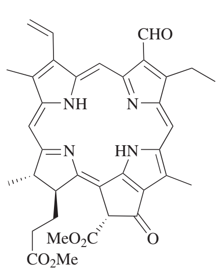
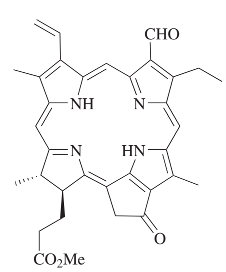
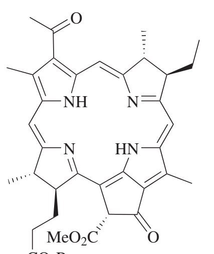
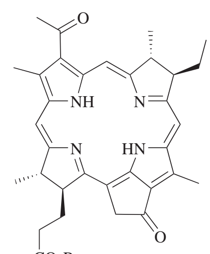
n	R		16β/16α	Refs.
3	MeO_2C	(48)	62:38	1524
3	CH_2=CH	(71)	85:15	1524
6	THPO	(41)[g]	84:16	1524
7	THPO	(69)	82:18	1524, 1525

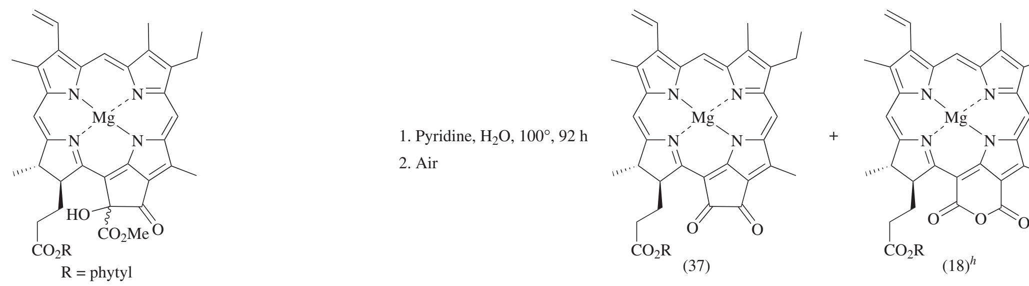
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24}			
	DMSO, H_2O, LiCl, 100°, 12 h	 **I** +  **II** **I** + **II** (69), **I/II** = 4:1	1526

C_{25} 	2,4,6-Collidine, $LiI{\bullet}xH_2O$, reflux, 3 h	 (77)	1527
C_{30} 	DMF, H_2O, LiCl, reflux, 20 h	 (64)	1528
C_{34} 	See table, reflux		

Solvent	Additive(s)	Time (h)		
Pyridine	—	5	(97)	1529
Pyridine	LiF	4	(78)	1530
Collidine	—	1.5	(98)	1531–1536
DMF	H_2O	1.5	(89)	1537
DMF	H_2O, NaCl	—	(67)	1537

TABLE 11A. DEALKOXYCARBONYLATIONS OF FIVE-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{34} 	Pyridine, H_2O, NaCl, 180°, 3 h	 (72)	1538
 R = phytyl	Collidine, reflux, 3 h	 (96)	1539



1540

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[a] The ring-opened product, $MeO_2C(CH_2)_3CH(Bn)CO_2Me$, was formed in 2.5% yield.

[b] The yield includes that of the preparation of the substrate.

[c] The substrate is a mixture of the 1- and 3-carbomethoxy isomers.

[d] The product contained the carboxylic acid instead of the methyl ester.

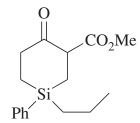
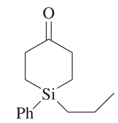
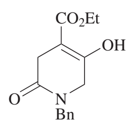
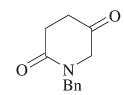
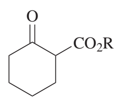
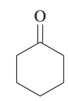
[e] The mixture was cooled immediately after this temperature was reached.

[f] Treatment of this mixture with NaOMe in MeOH/THF at rt for 17 h produced a 17:1 mixture of isomers **I** and **II**.

[g] The number is the yield of the β-isomer obtained by chromatography of the crude product mixture.

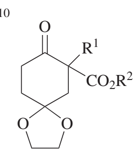
[h] This product contained some unreacted substrate.

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS

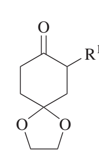
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	DMSO, H_2O, NaCl, reflux	 (91)	1541
	DMSO, H_2O, LiCl, 150°, 3.5 h	 (24)	1542
C_7 	See table.		

R	Solvent	Additive(s)	Temp	Time		Refs.
Me	dioxane	H_2O, Al_2O_3	reflux	27 h	(90)	310
Me	*o*-xylene	DABCO	reflux	4 h	(>96)	297
Et[a]	DMF	H_2O	134–135°	3 h	(64)	332
Et[a]	DMSO	H_2O	189º	3 h	(87)	332
Et	none	H_2O, LiBr, $(n\text{-Bu})_4NBr$	Mw (30 W), 138°	8 min	(96)	129
Et	dioxane	H_2O, Al_2O_3	reflux	73 h	(80)	310
Et	*o*-xylene	DABCO	reflux	4 h	(>96)	297
Et	HMPA	$MgCl_2$	140–150°	1 h	(84)	109

C_{7-10}

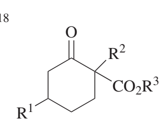


See table.

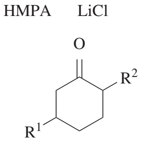


R^1	R^2	Solvent	Additive	Temp (º)	Time (h)		Refs.
H	Et	HMPA	$MgCl_2$	150	2	(92)	109
Me	Me	DMF	LiI	130	6	(86)	1543
CH_2=$CHCH_2$	Me	DMF	LiI	130	6	(90)	1544
CH_2=$CHCH_2$	Me	HMPA	LiCl	130	8	(91)	1545

C_{7-18}



See table.



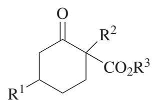
Continued on next page.

R^1	R^2	R^3	Solvent	Additive(s)	Temp	Time		Refs.
H	HO	Me	MeCN	H_2O, MgI_2	81º	2 h	(84)	1327
H	Me	Me	DMF	LiCl	145–150º	7 h	(—)	1546
H	Et	Et	DMSO	H_2O, $CaCl_2$	150º	—	(20)	129
H	Et	Et	none	H_2O, LiBr, $(n\text{-Bu})_4NBr$	Mw (30 W), 160º	15 min	(94)	129
H	Et	Et	none	H_2O, LiBr, $(n\text{-Bu})_4NBr$	160º	3 h	(60)	129
H	*i*-Pr	Et	DMF	LiI•$2H_2O$	reflux	45 h	(91)	1547
Me	*i*-Pr	Me	DMF	LiCl	145–150º	7 h	(—)	1546
H	$NC(CH_2)_2$	Et	MeCN	NaI, $AlCl_3$	reflux	5 h	(67)	1548
H	*n*-Bu	Et	none	H_2O, LiBr, $(n\text{-Bu})_4NBr$	Mw (45 W), 167º	20 min	(89)	129
H	CH_2=$CH(CH_2)_2$	Et	DMSO	H_2O, LiCl	reflux	2 h	(72)	1549
H	$CH\equiv C(CH_2)_2$	Et	DMF	LiI	150º	1.5 h	(—)	1550
H	$NC(CH_2)_3$	Et	DMSO	H_2O, LiCl	reflux	6 h	(65)	1551
H	2-furyl	Me	NMP	H_2O, LiCl	reflux	5 h	(53)	1385, 237

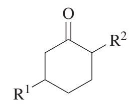
TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.

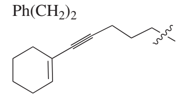
C_{7-18}



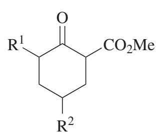
See table.



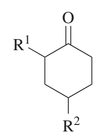
Continued from previous page.

R^1	R^2	R^3	Solvent	Additive(s)	Temp	Time		Refs.
H	n-C_6H_{13}	Et	none	H_2O, LiBr, $(n\text{-Bu})_4NBr$	Mw (90 W), 186°	20 min	(87)	129
H	Bn	Me	DMF	LiCl	145–150°	7 h	(90)	1546
H	$4\text{-MeOC}_6H_4CH_2$	Me	DMF	LiCl	145–150°	7 h	(—)	1546
H	$2\text{-IC}_6H_4CH_2$	Me	DMF	LiI	150°	7 h	(65)	1552
H	$Ph(CH_2)_2$	Me	DMF	LiCl	145–150°	7 h	(—)	1546
H		Et	DMF	LiI	150°	7 h	(86)	1553

C_{7-11}

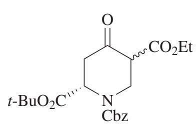


See table.

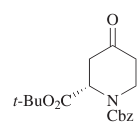


R^1	R^2	Solvent	Additives	Temp (°)	Time		Refs.
H	PhSe	DMSO	H_2O, NaCl	—	—	(61)	257
H	t-Bu	PhMe	DMAP, phosphate buffer	90	8 d	(61)	87
TBSO	H	DMSO	H_2O, NaCl	130	30 min	(100)	1554

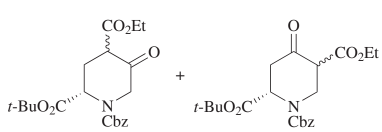
C_7



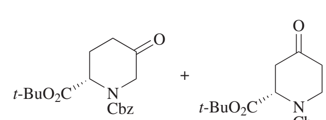
DMSO, H_2O, NaCl, 140°, 4 h



(75) 1555



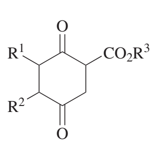
DMSO, H_2O, NaCl, 140°, 4 h



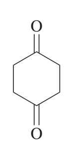
I **II**

I + **II** (75), **I/II** = 1.5:1 1556, 1557

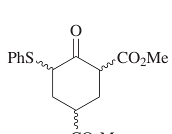
C_8



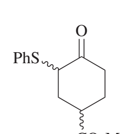
See table.



R^1	R^2	R^3	Solvent	Additive	Temp (°)	Time (h)		Refs.
H	MeO_2C	Me	DMSO	H_2O	reflux	48	(60)	15
H	EtO_2C	Et	H_2O	—	200	0.5	(100)	1154, 1558–1560
EtO_2C	H	Et	H_2O	—	230–240	—	(—)	1561

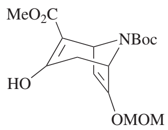
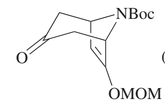
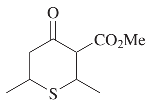
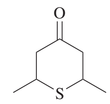
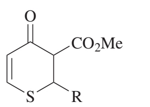
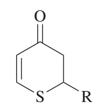
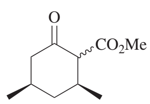
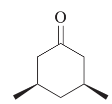
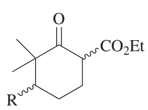
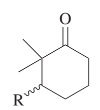


DMSO, NaCl, 150°, 4.5 h



(80) 1562

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	DMSO, H_2O, 150°	 (90)	1563
	H_2O, H_2, 13.6 atm, 200°, 12 h	 (—)	1564
$C_{8–12}$			
	DMF, $MgCl_2$, 12-c-4, phosphate buffer, 160°, 16 h	 R: Et (—); *i*-Pr (—); *n*-Bu (60); Ph (68)	125
C_9			
	DMSO, H_2O, NaCl, 170°, 2 h	 (79)	1565
	DMSO, H_2O, NaCl, 180–185°, 3.5 h	 R, Config.: D (*R*) (55); AcO (*S*) (79)	1566, 1567; 1568

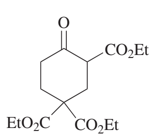
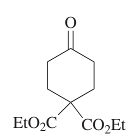
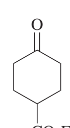
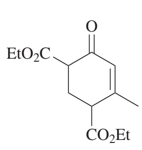
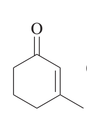
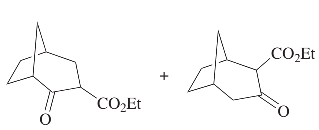
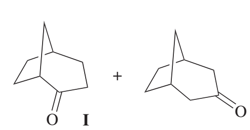
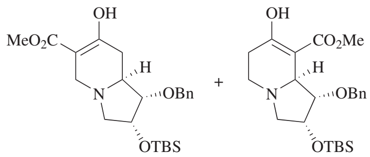
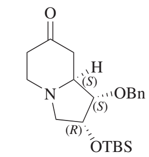
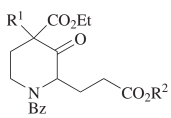
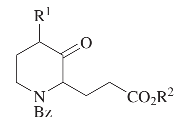
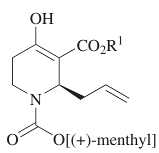
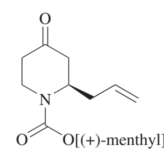
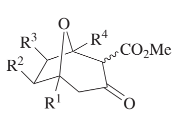
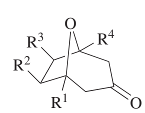
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 150–160°, 2 h	 (83)	83
	DMSO, H_2O, pyridine, LiCl, 165°, 13 h	 (72)	83
	H_2O, 160°	 (—)	1569
	H_2O, 230°, "several" h	 **I** + **II** (—), **I/II** = 51:49	1570

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

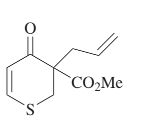
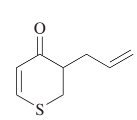
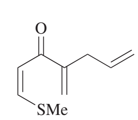
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, H_2O, NaCl, 130–140°, 4 min	 (92)	1571
C_{9-10} 	DMSO, H_2O, additive		1572
C_9 	DMSO, H_2O, NaCl		1573

R^1	R^2	Additive	Temp (°)	Time (h)	
H	H	NaCl	155–160	3	(75)
H	Et	NaCl	155–160	3	(67)
Me	Et	LiCl	165	10	(71)

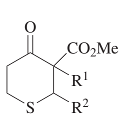
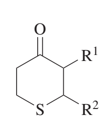
R^1	
Me	(80)
Et	(—)[b]

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 	DMSO, H_2O, additive		

R^1	R^2	R^3	R^4	Additive	Temp (°)	Time (h)		Refs.
Me	H	H	H	LiCl	reflux	2.5	(78)	1574
Me	H	PhS	H	NaCl	140	1.5	(73)	1575
Me	PhS	H	H	NaCl	140	1.5	(78)	1575
$PhSCH_2$	H	Me	H	NaCl	140	1.5	(71)	1575
$PhSCH_2$	H	H	Me	NaCl	140	1.5	(72)	1575

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMF, additive, LiI, reflux, 8 h	 **I** +  **II**	125

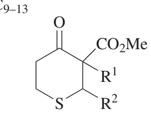
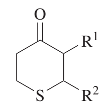
Additive	**I**	**II**
H_2O	(66)	(9)
—	(5)	(59)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-13} 	See table.		

R^1	R^2	Solvent	Additive(s)	Temp	Time		Refs.
n-Pr	H	H_2O	—	—	—	—	1576
$CH_2{=}CHCH_2$	H	DMSO	LiI, NaCN	reflux	—	(0)	124
$CH_2{=}CHCH_2$	H	DMSO	H_2O, NaCl	reflux	—	(41)	124
$CH_2{=}CHCH_2$	H	DMSO	$MgCl_2{\bullet}6H_2O$	reflux	—	(23)	124
$CH_2{=}CHCH_2$	H	HMPA	NaCN	50°	—	(45)	124
$CH_2{=}CHCH_2$	H	DMF	LiI	reflux	—	(4)	124
$CH_2{=}CHCH_2$	H	DMF	H_2O, LiI	reflux	12 h	(87)	124
$CH_2{=}CHCH_2$	H	dioxane	Al_2O_3	reflux	—	(0)	124

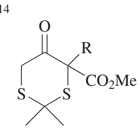
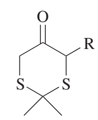
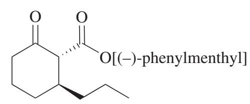
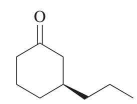
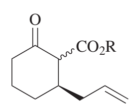
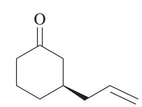
Continued on next page.

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

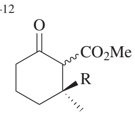
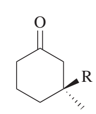
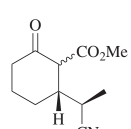
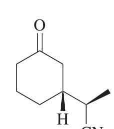
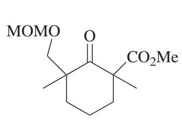
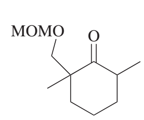
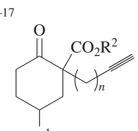
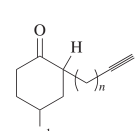
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-13} 	See table.		

Continued from previous page.

R^1	R^2	Solvent	Additive(s)	Temp	Time		Refs.
CH_2=CHCH$_2$	*n*-Bu	DMF	H_2O, LiI	reflux	20 h	(68)	124
n-C_5H_{11}	H	DMSO	H_2O, NaCl	150°	20 h	(46)	1577
n-C_5H_{11}	H	HMPA	LiCl	65–75°	20 h	(65)	1578
CH_2=CH(CH_2)$_3$	H	DMSO	H_2O, LiI	reflux	3–5 d	(29)	1579
CH_2=CH(CH_2)$_4$	H	DMSO	H_2O, LiI	reflux	3–5 d	(48)	1579
Bn	H	DMSO	H_2O, NaCl	150°	20 h	(60)	1578, 1577

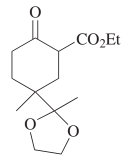
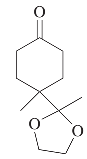
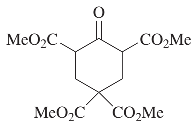
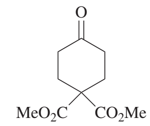
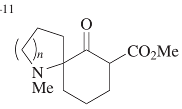
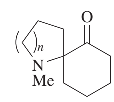
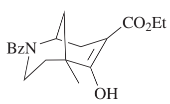
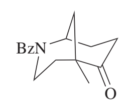
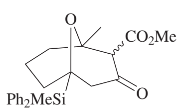
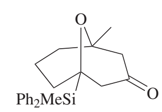
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-14} 	DMSO, H_2O, NaCl, 135–140°, 5–8 h	 R: Et (69); CH_2=CHCH$_2$ (48); *n*-Bu (90); $MeO_2C(CH_2)_4$ (81); Bn (49)	1580
C_{10}  85.0:15.0 er	DMSO, H_2O, NaCl, reflux, 20 h	 (59) 91.5:8.5 er	101
	DMSO, H_2O, NaCl		

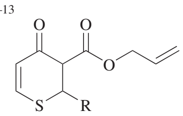
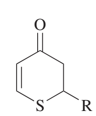
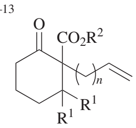
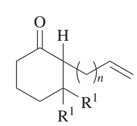
R	er	Temp (°)	Time (h)		Refs.
Me	95.0:5.0	150	3	(89)	1581
(–)-menthyl	—	165	4	(67)	102

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-12} 	DMSO, H_2O, NaCl, 150°, 3 h	 R, er: Et (93) 95.5:4.5; *i*-Pr (—) 93.0:7.0; *n*-Bu (—) 94.5:5.5	190
C_{10} 	DMSO, H_2O, NaCl, 165°, 2 h	 (83)	1477
	HMPA, LiCl, 120°, 2 h	 (40)	61
C_{10-17} 	See table.		

n	R^1	R^2	Solvent	Additive	Temp (°)	Time (h)		Refs.
1	H	Et	2,4,6-collidine	LiI•2H_2O	180	—	(54)	1582
3	H	Me	DMF	LiI	150	1.5	(87)	356, 357
3	H	Et	DMF	LiI	130–150	2	(—)	1360
3	*i*-Pr	Et	DMF	LiI	"heat"	—	(—)	1583
4	H	Et	DMF	LiI	130–150	2	(—)	1360

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	DMSO, H_2O, NaCl, 170–180°, 6 h	 (85)	1584
	H_2O, 200°, 30 min	 (100)	973
C_{10-11} 	DMSO, H_2O, KCl, 115–120°, 3 h	 *n* 1 (73) 2 (56)	1585
C_{10} 	DMSO, H_2O, NaCl, 155–160°, 3 h	 (74)	1586
	DMSO, H_2O, LiCl, 130°, 2 h	 (91)	1587

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-13} 	DMF, additive, $MgCl_2$•$6H_2O$, reflux		97
C_{11-13} 	See table.		

R	Additive	Time (h)	
n-Bu	—	20	(91)
Bn	phosphate buffer	16	(79)

n	R^1	R^2	Solvent	Additive	Temp (°)	Time (h)		Refs.
1	Me	Me	2,4,6-collidine	LiI•$2H_2O$	reflux	19	(56)	1588
2	H	Et	DMSO	NaCN	160	8.5	(70)	1358
3	H	Et	DMF	LiI	130–150	2	(—)	1360
4	H	Et	DMF	LiI	130–150	2	(—)	1360

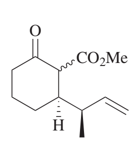
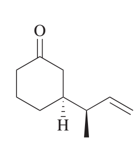
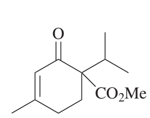
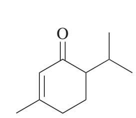
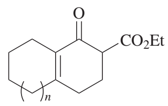
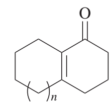
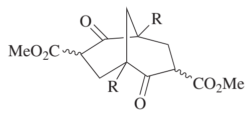
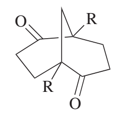
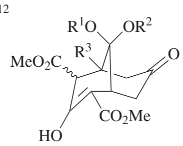
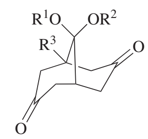
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl, 160°, 5 h	 (79)	1412
	Collidine, LiI, reflux, 6 h	 (81)	1589

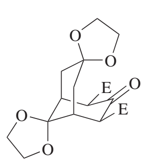
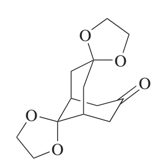
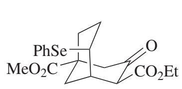
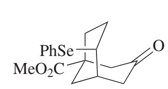
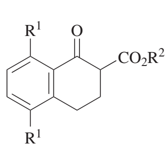
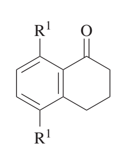
TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-17} 	DMF, H_2O, LiI, 155°, 7 h	 n: 1 (77); 2 (84); 3 (90); 7 (84)	1590
C_{11-13} 	See table.		

R	Solvent	Additive	Temp (°)	Time (h)		Refs.
H	H_2O	—	170–180	1.5	(100)	973, 1154
MeO_2C	H_2O	—	170–180	—	(100)	973, 1154
MeO_2C	*o*-xylene	DABCO	85–92	1	(67)	297

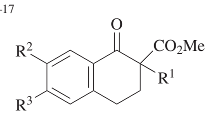
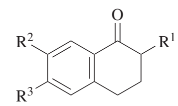
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12} 	DMSO, H_2O, NaCl		

R^1	R^2	R^3	Temp (°)	Time (h)		Refs.
Me	Me	H	170	—	(67)	1591
—$(CH_2)_2$—		H	170	—	(79)	1591, 1592
Me	Me	MeO_2C	170; then 190	1.5; 0.5	(56)	1593

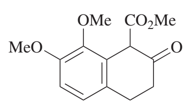
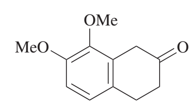
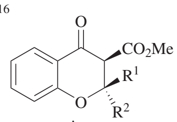
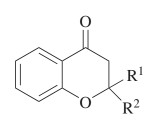
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}  E = CO_2Me	DMSO, H_2O, NaCl, 100–110°, 3 h	 (92)	192
	DMSO, H_2O, 150°, 3.25 h	 (74)	1594
	See table.		

R^1	R^2	Cond.		Refs.
H	Me	H_2O, Dowex-50, reflux, 12 h	(85)	1595
Cl	Et	H_2O, 17 bar, 240°, 2.5 h	(75)	1596

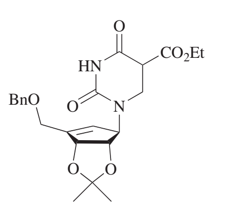
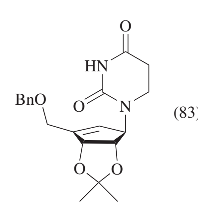
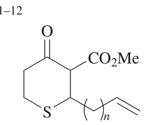
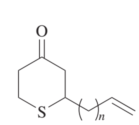
TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-17} 	See table.		

R^1	R^2	R^3	Solvent	Additives	Temp	Time (h)		Refs.
HO	H	H	MeCN	H_2O, MgI_2	81°	2	(81)	1327
2-furyl	H	H	DMF	H_2O, HOAc, LiCl	reflux	5	(72)	237, 1385
2-furyl	H	MeO	DMF	H_2O, HOAc, LiCl	reflux	5	(80)	237, 1385
2-furyl	H	MeO	NMP	H_2O, HOAc, LiCl	reflux	5	(69)[c]	237, 1385
2-furyl	MeO	MeO	DMF	H_2O, HOAc, LiCl	reflux	5	(82)	237, 1385
Ph	H	F	DMF	H_2O, LiCl	150°	2.5	(87)	1597

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl, 130°, 2.5 h	 (73)	1598
C_{11-16}  racemic	DMSO, H_2O, NaCl, 155°, 4 h		

R^1	R^2		Refs.
H	Me	(77)[d]	1599
Me	Me	(86)[d]	1599, 1600
H	Ph	(89)	1599

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	DMSO, H_2O, NaCl, reflux, 1 h	 (83)	1125
C_{11-12} 	DMF, H_2O, LiI, reflux, 3–5 d		1579

n	
3	(88)[e]
4	(85)[e]

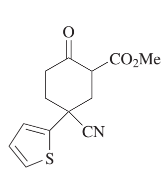
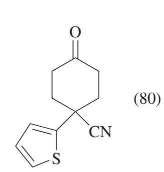
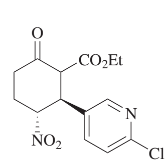
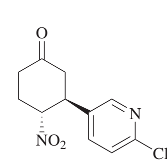
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	DMSO, H_2O, NaCl, 150°, 5 h	 (80)	1601
	DMSO, H_2O, LiCl, "heat"	 (48)	1602

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

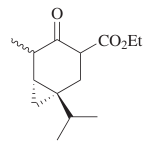
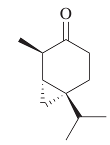
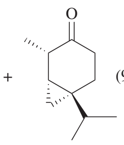
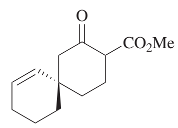
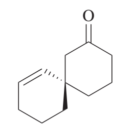
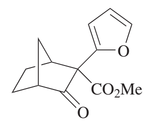
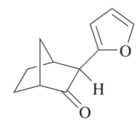
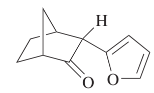
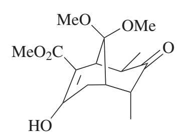
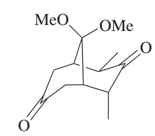
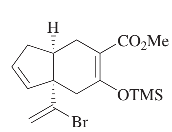
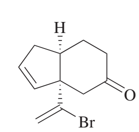
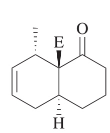
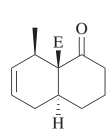
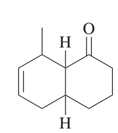
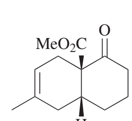
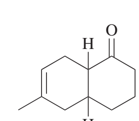
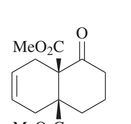
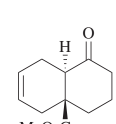
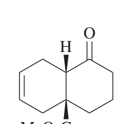
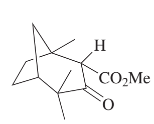
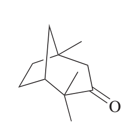
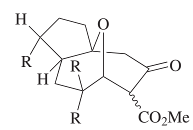
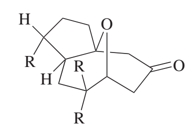
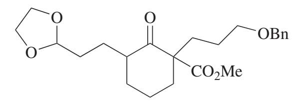
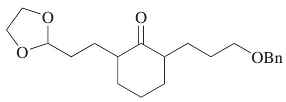
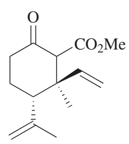
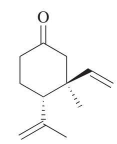
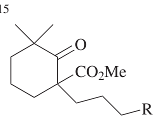
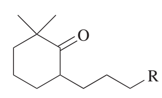
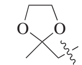
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	DMSO, H_2O, NaCl, 140°, 4 h	 (87) +  (9)	1603
	DMSO, H_2O, NaCl, 160°, 6 h	 (95)	1604
	DMF, H_2O, LiCl, HOAc, reflux, 5 h	 (46) +  (38)	1386
	DMSO, H_2O, NaCl, 170°, 1.5 h; then 190°, 0.5 h	 (0)[f]	1593
	DMSO, H_2O, NaCl, reflux, 4 h	 (71)[e]	193
 +  I I/II = 5:4 II E = CO_2Me	2,4,6-Collidine, H_2O, LiI, reflux, 90 min	 (82) 3 isomers	1605
	2,4,6-Collidine, H_2O, LiI, reflux, 16 h	 (40)	1606
	DMSO, H_2O, NaCl, 150°	 I +  II I + II (—), I/II = 2:1	54, 53
	2,4,6-Collidine, LiI•$2H_2O$, reflux, 8 h	 (86)	1607

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{12\text{–}15}$			
	DMSO, H_2O, NaCl, 140°, 90 min	 R: H (56); Me (84)	1608
C_{13}			
	DMSO, $MgCl_2$, reflux, 6 h	 (78)	1609
	DMSO, H_2O, NaCl, 150°, 4 h	 (54)[e]	1610
$C_{13\text{–}15}$			
	DMSO, $MgCl_2$•$6H_2O$, 160°, 4 h	 R: EtO_2C (31)[e]	1611, 1612
		R:  (43)	1611

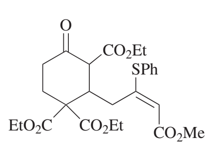
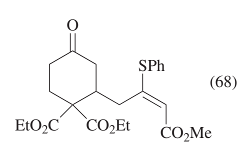
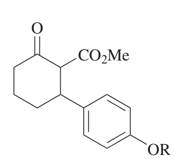
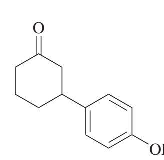
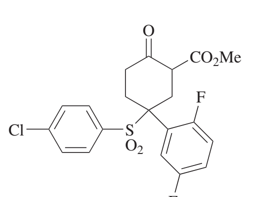
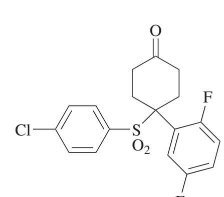
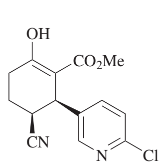
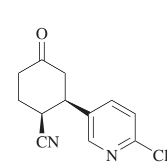
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	DMF, LiI, 125–130°, 2.5 h	 (68)	979
	DMSO, LiBr, 180°, 40 min	 R: H (80); Me (98)	1613
	DMSO, H_2O, NaCl, 150°	 (30)	1614
	DMSO, H_2O, 130°, 24 h	 (99)	1615

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

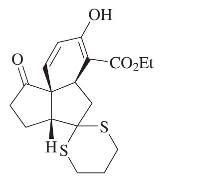
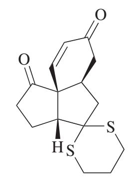
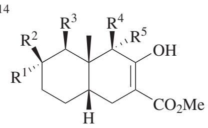
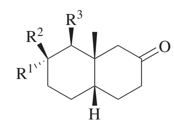
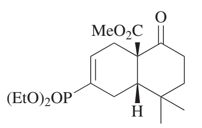
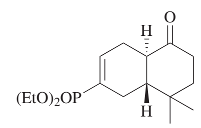
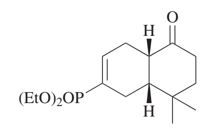
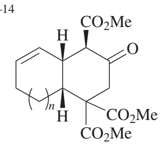
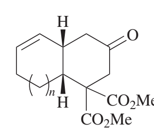
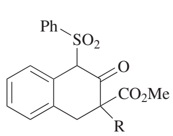
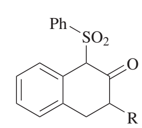
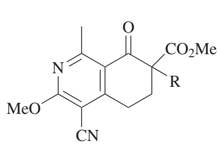
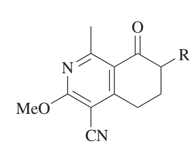
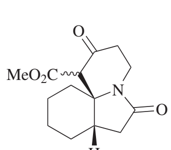
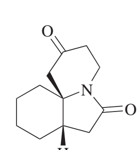
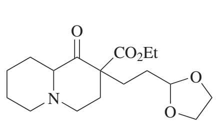
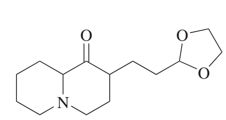
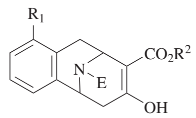
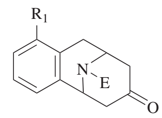
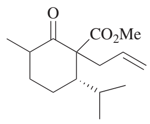
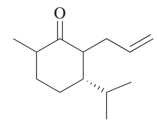
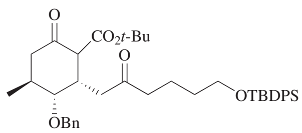
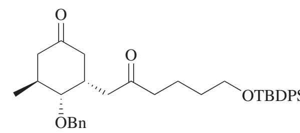
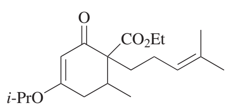
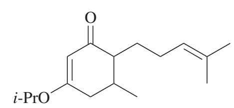
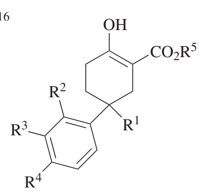
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	DMF, H_2O, NaCl, reflux, 5 h	 (89)	1616, 273
C_{13-14} 	DMSO, H_2O, NaCl	 (—) R^1 R^2 R^3 R^4 R^5 H H Me MeO_2C H =O H H MeO_2C =O H MeO_2C H	1617
C_{13} 	2,4,6-Collidine, LiI•$2H_2O$, reflux	 +  **I** **I + II** (70), **I/II** = 6:1 **II**	1618
C_{13-14} 	DMSO, H_2O	 *n* Temp (°) Time (h) 1 150 15 (68) 2 140 2 (80)	84
	DMSO, NaBr, 60–70°, 1 h	 R Et (72)[e] allyl (61)[e]	1619
	DMSO, H_2O, NaCl, 145–150°, 6 h	 R Me (44) Et (43)	1620
C_{13} 	DMSO, *t*-BuSH, $MgCl_2$, 130°, 3.5 h	 (76)	1621
	DMSO, H_2O, LiCl, 170°, 4 h	 (88)	1622

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

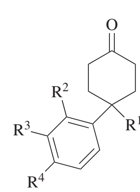
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}  E = CO_2Me	DMSO, H_2O, LiCl, 130°, 8 h		1623
C_{14} 	DMSO, NaCN, 160°, 2 h	 (92)	1624
	DMSO, H_2O, NaCl, 140°, 2 h	 (—)	1625
	DMPU, LiI, 130°, 48 h	 (45)	1626

R^1	R^2	
H	Me	(46)
Br	Et	(62)
O_2N	Et	(44)

$C_{14–16}$



DMSO, additive, NaCl



R^1	R^2	R^3	R^4	R^5	Additive	Temp (°)	Time (h)		Refs.
NC	H	H	H	Me	H_2O	130	2	(68)	1627, 1628
NC	F	H	H	Me	—	150	—	(—)	1628
NC	H	F	H	Me	—	150	—	(—)	1628
NC	H	H	F	Me	—	150	—	(—)	1628
NC	F	F	H	Me	—	150	—	(—)	1628
NC	H	Cl	Cl	Me	—	150	—	(—)	1628
NC	Cl	H	H	Me	—	150	—	(—)	1628
NC	Cl	Cl	H	Me	—	150	—	(—)	1628
NC	H	H	F	Me	H_2O	150	2–6	(53)	1629
NC	CF_3O	H	H	Me	—	150	—	(—)	1628
NC	H	MeO	MeO	Me	H_2O	140	6	(87)	1631
NC	H	–OCH_2O–		Et	H_2O	—	—	(95)	1632
NC	H	*c*-C_5H_9O	MeO	Me	H_2O	150–160	5	(83)	1633, 1634
NC	H	MeO_2C	H	Me	—	150	—	(—)	1628
NC	CF_3	H	H	Me	—	150	—	(—)	1628
NC	H	CF_3	H	Me	—	150	—	(61)	1628
NC	H	CHF_2	CHF_2	Me	H_2O	140–145	48	(64)	1630
MeO_2C	H	H	F	Me	H_2O	150	2–6	(75)	1629
MeO_2C	H	H	O_2N	Me	H_2O	130; then 150–155	2; 2.5	(76)[g]	1635

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

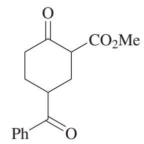
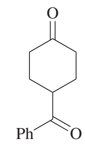
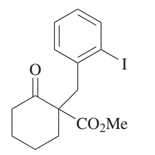
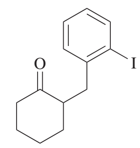
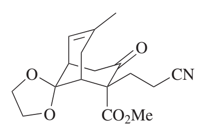
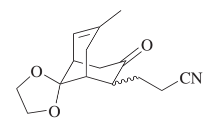
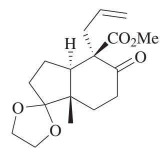
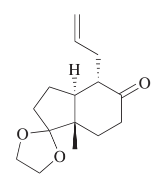
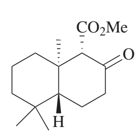
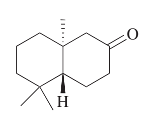
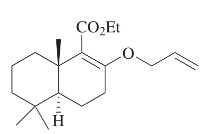
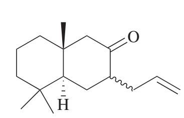
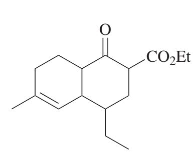
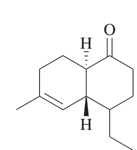
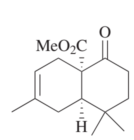
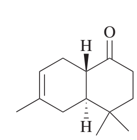
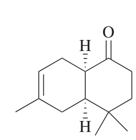
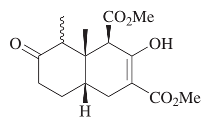
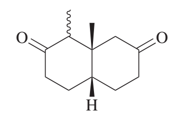
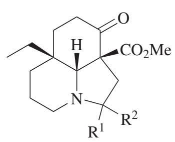
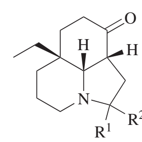
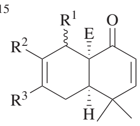
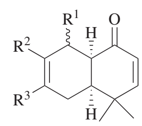
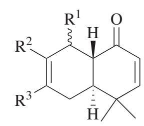
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	DMSO, H_2O, NaCl, 150°	 (70)	1636
	DMF, LiI, 150°, 7 h	 (65)	1552
	DMF, LiBr, 150°, 15 h	 (87)	1592, 1637
	DMF, H_2O, LiCl, 150°, 8 h	 (99)	62
	DMF, KI, reflux, 5 h	 (5)	1638
	DMSO, $CaCl_2$•$2H_2O$, reflux	 (—)	107
	1. DMSO, H_2O, NaCl, 158–170°, 5 h 2. NaOMe	 (82)	1639
	2,4,6-Collidine, H_2O, LiI, reflux, 2.5 h	 **I** +  **II** **I + II** (86), **I/II** = 9:1	1640

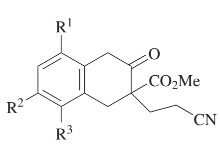
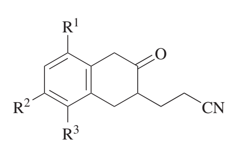
TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	DMSO, H_2O, NaCl, reflux, 18 h	 (62)	1617
	DMF, LiCl		1641, 1642

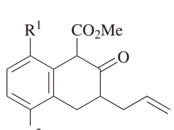
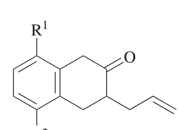
R^1	R^2	Temp (º)	Time		Refs.
H	H	140	3 h	(88)	1641, 1642
=O		145	overnight	(75)	

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14-15}  E = CO_2Me	2,4,6-Collidine, additive	 **I** +  **II**	

R^1	R^1 Config.	R^2	R^3	Additive	Temp	Time (h)	**I**	**II**	Refs.
H	—	Me	H	$LiI{\bullet}2H_2O$	reflux	3	(38)	(38)	1640
H	—	H	Me	$LiI{\bullet}2H_2O$	reflux	3	(49)	(49)	1640
Me	α	H	H	LiI, H_2O	"heat"	1.5	(20)	(44)	1643
Me	β	H	H	LiI, H_2O	reflux	1	(66)	(0)	1643
Me	α	H	Me	LiI, H_2O	reflux	1.5	(46)	(37)	1643
Me	β	H	Me	LiI, H_2O	reflux	1.5	(24)	(11)	1643

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	HMPA, additive(s)		

R^1	R^2	R^3	Additive(s)	Temp (º)	Time		Refs.
H	MeO	MeO	LiCl	75–80	23 h	(35)	1644
H	MeO	MeO	H_2O, NaCN	75	50 min	(35)	1644
MeO	H	H	LiCl	75	20 h	(68)	1645

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, LiCl		

R^1	R^2	Temp (º)	Time (h)		Refs.
H	H	150	1	(83)	1646, 1647
H	MeO	150	4	(100)[e]	1648, 1647
MeO	H	125	5	(94)	1649

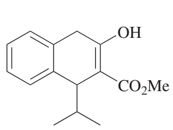
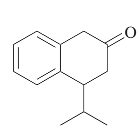
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, LiCl, reflux, 3 h	 (81)	1650

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

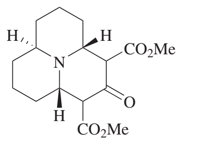
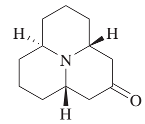
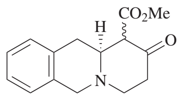
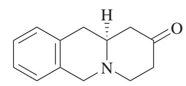
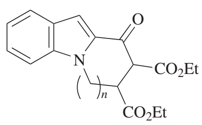
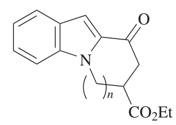
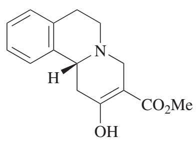
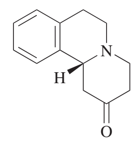
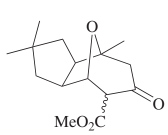
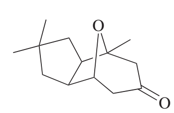
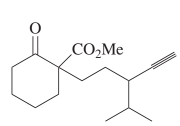
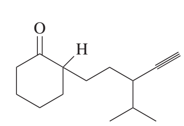
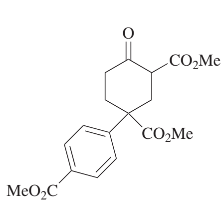
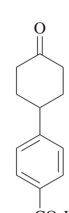
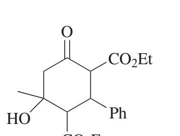
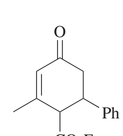
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	DMF, H_2O, NaCl, reflux, 4 h	 (56)	275
 >95.0:5.0 er	DMF, H_2O, additive, heat	 Additive / er: NaCl (29) 55.5:44.5; LiCl (7) 59.5:40.5	75
C_{14-15}			
	$B(OH)_3$	 *n* / Temp (°) / Time (h): 1, 150, 1.25 (64); 2, 150; then 170, 1; 3 (75)	318
C_{14}			
	DMSO, H_2O, NaCl, 140°, 3 h	 (60)	1651
	DMSO, H_2O, NaCl, 140°, 16 h	 (65)	1652
C_{15}			
	DMF, LiI, 150°, 1.5 h	 (75)	356, 357
	DMSO, H_2O, NaCN, 180–185°, 2 h	 (73)	1653
	H_2O, 135°, 10 h	 (45)	1654

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

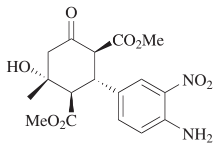
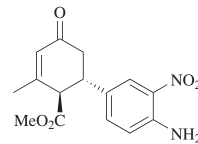
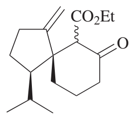
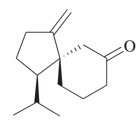
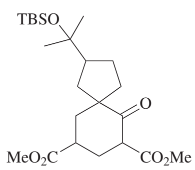
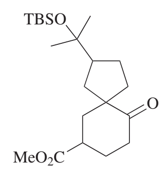
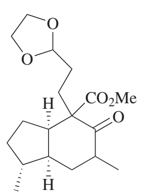
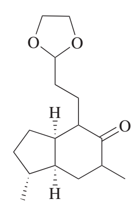
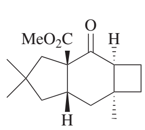
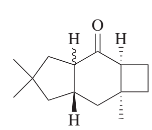
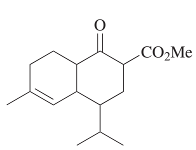
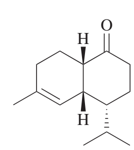
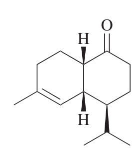
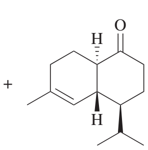
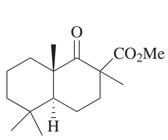
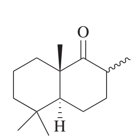
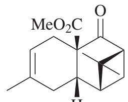
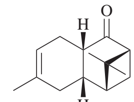
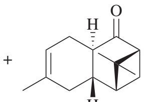
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	*N*-Methylpiperazine, EtOH, reflux, 1 h	 (70)	1655
	DMSO, NaCl, 130°, 2 h	 (70)	1656
	DMSO, H_2O, NaCl, 150°, 4.5 h	 (81)	1657
	DMF, LiI, reflux, 2 h	 (64)	1658
	HMPA, LiCl, 90°, 20 h	 (82)	1659
	DMSO, H_2O, NaCl, "heat"	 (56) +  (23) +  (21)	1660
	HMPA, H_2O, NaCl, 120°, 10 h	 (46)[h]	1661
	2,4,6-Collidine, LiI, H_2O, reflux, 2.3 h	 (80) +  (6)	1662

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

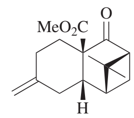
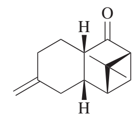
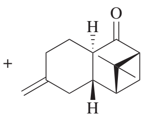
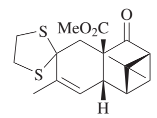
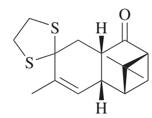
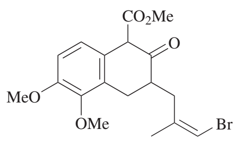
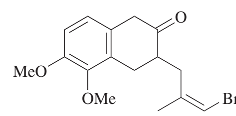
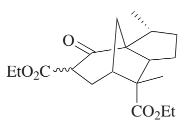
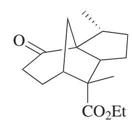
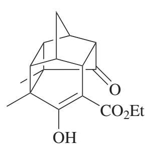
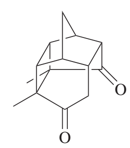
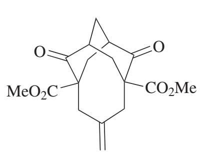
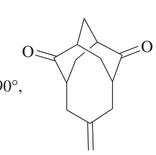
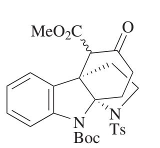
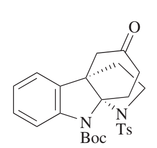
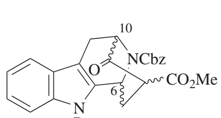
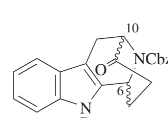
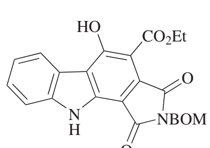
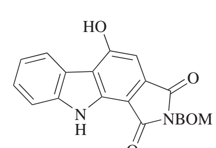
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	2,4,6-Collidine, LiI, H_2O, reflux, 3.5 h	 (8) +  (72)	1662
	2,4,6-Collidine, LiI, H_2O, reflux	 (91)	1663
	DMSO, H_2O, LiCl, 150°, 20 min	 (80)[e]	271
	DMSO, $MgCl_2$•$6H_2O$, 140°, 28 h	 (74)[e]	1664, 1665
	DMSO, H_2O, NaCl, 150°, 4 h	 (91)	1666
	DMSO, CaI_2•$4H_2O$, 185–190°, 7 h; then distill volatiles	 (64)	1667
	DMSO, H_2O, LiCl, 130°, 7 h	 (87)	191
	DMF, H_2O, NaCl, 130°, 8 h	 R / C-6,10 Config. Me / (*S*,*S*) / (73) Me / (*R*,*R*) / (—) Bn / (*S*,*S*) / (68)	1668, 1669
	DMF, LiCl, reflux, 18 h	 (96)	1670

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

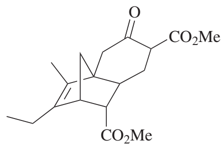
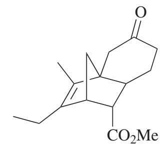
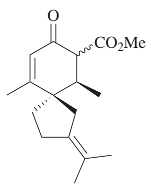
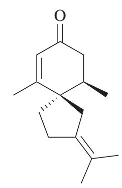
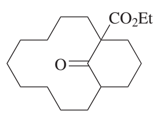
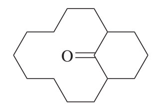
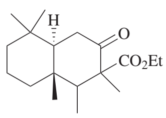
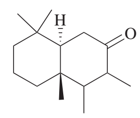
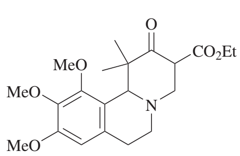
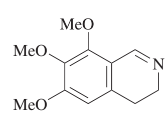
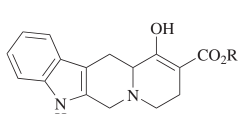
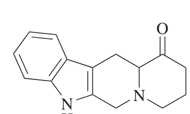
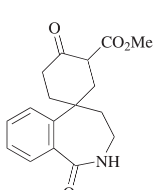
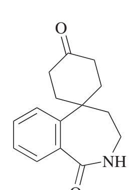
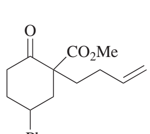
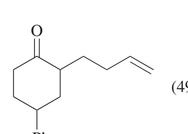
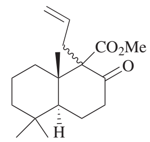
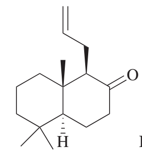
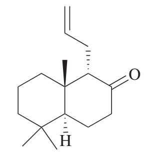
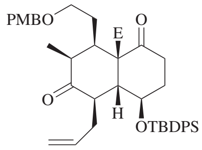
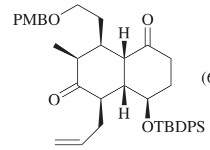
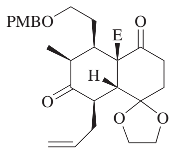
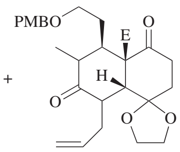
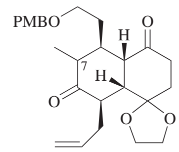
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	DMSO, H_2O, LiCl, 160°, 1 h	 (75)	1671
 63:37 dr	DMSO, H_2O, NaCl, 150°, 4.5 h	 (77) 63:37 dr	1657
	DMF, LiCl, 130°, 4 h	 (88)	1672
	DMSO, H_2O, NaCl, 170–180°, 2 h	 (60)	1673
	DMSO, H_2O, LiCl, 100°, 4 h	 (80)	1674
 R = mixture of Me and Et	DMSO, NaCl, 150°, 20 h	 (58)	1675
	DMF, H_2O, NaCl, 150°, 3 h	 (86)	1676
C_{17}			
	DMSO, H_2O, LiCl	 (49)	1677

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	$CaCl_2$•$2H_2O$, reflux	 **I** +  **II**	
		Solvent / Time (h) / I + II / I/II	
		DMSO / 1.25 / (70) / 86:14	107
		DMSO / 2 / (100) / —	1678
		NMP / — / (91) / 86:14	106
 E = CO_2Me	DMF, H_2O, LiCl, 150°, 10 h	 (64)	1679
 +  **I** **I/II** = 3:1 **II**; E = CO_2Me	DMF, H_2O, LiCl, 150°, 10 h	 (35)[i]	1679

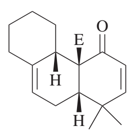
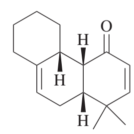
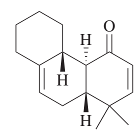
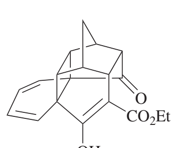
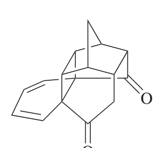
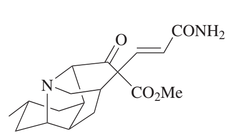
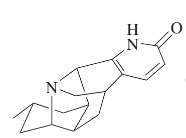
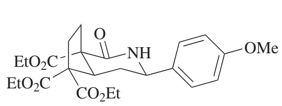
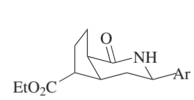
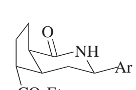
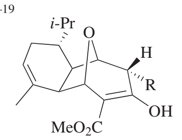
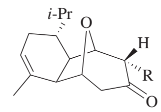
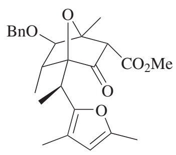
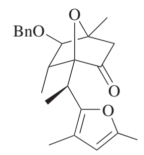
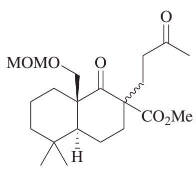
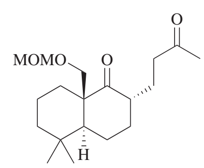
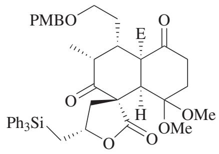
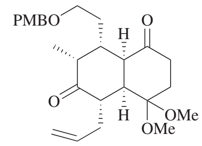
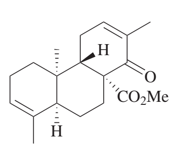
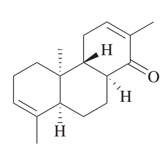
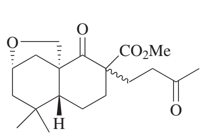
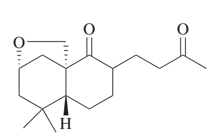
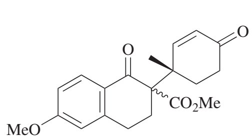
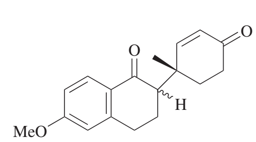
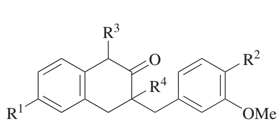
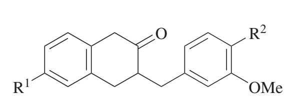
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
 E = CO_2Me	2,4,6-Collidine, H_2O, reflux, 1.5 h	 (29) +  (32)	1643
	DMSO, H_2O, NaCl, 150–160°, 6 h	 (56)	1680
	MeCN, $Me_4N^+AcO^-$, 135°, 16 h	 (71)	267
	DMF, H_2O, LiCl, reflux, 18 h	 (36) +  (25); Ar = 4-$MeOC_6H_4$	64

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17-19} 	DMSO, H_2O, LiCl, 130°, 4 h	 R Me (90) allyl (86)	1681
C_{17} 	PhMe, Et_3N, reflux, 3 d	 (47)	1682
C_{18} 	HMPA, LiCl, 120–140°, 8 h	 Substrate [j] crystalline isomer (84) oily isomer (82)	60
 E = $CO_2(CH_2)_2TMS$[k]	THF, $(n\text{-}Bu)_4NF$, rt, 10 h	 (60) 90.0:10.0 er	52
	H_2O, pyridine (99:1), 230°, 22 h	 (92)	1683
	HMPA, LiCl, 140–150°	 (82)	1684
	HMPA, $Me_4N^+AcO^-$, 95°, 6 h	 (87)	1685
	DMF, LiI•$3H_2O$, reflux, 3 h		1686

R^1	R^2	R^3	R^4	
H	H	H	EtO_2C	(55)
H	MeO	H	EtO_2C	(58)
MeO	MeO	H	EtO_2C	(19)
H	H	MeO_2C	H	(33)
H	MeO	MeO_2C	H	(30)
MeO	MeO	MeO_2C	H	(35)

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

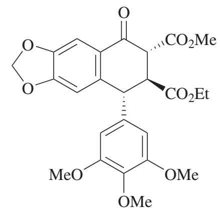
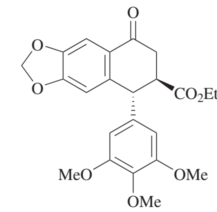
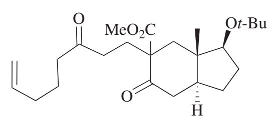
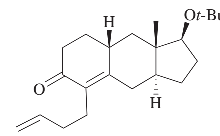
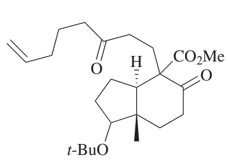
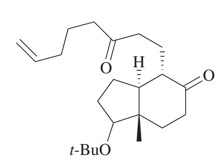
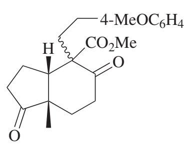
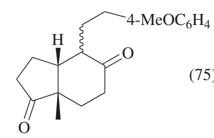
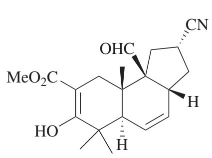
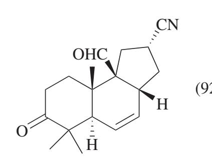
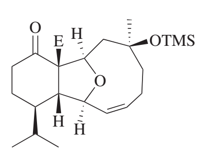
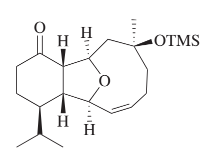
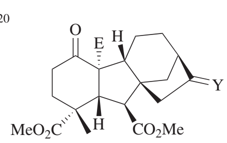
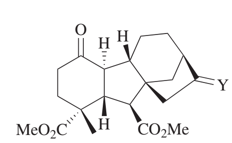
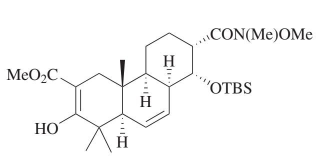
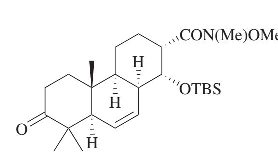
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	HOAc, KOAc, reflux, 14 h	 (100)	1687
C_{19} 	1. DMF, LiCl, reflux, 16 h [l] 2. NaOH, EtOH, reflux, 30 min	 (75)	1688
	HMPA, H_2O, NaI, 160°	 (68)	1689
	HMPA, NaI, 160°, 22 h	 (75)	1690
	DMSO, H_2O, 155°, 2.5 h	 (92)	277
 E = CO_2Me	DMF, H_2O, NaBr, 120°, 42 h	 (76)	1691
C_{19-20}  E = CO_2Me	1. Conditions 2. CH_2N_2		
	Y: O — Conditions 1: 2,4,6-collidine, LiI, reflux, 65 h	(—)	1692
	Y: CH_2 — Conditions 1: HMPA, *n*-PrSNa, rt, overnight [m]	(20)	1693
C_{19} 	DMSO, H_2O, 150°	 (86)	1694

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

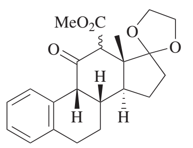
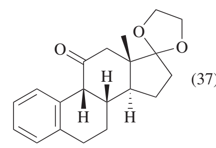
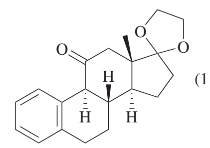
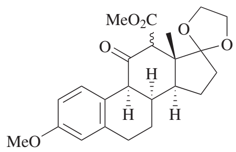
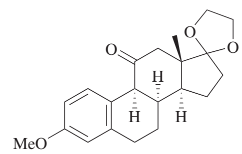
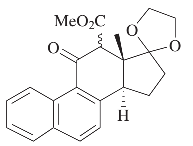
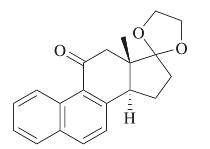
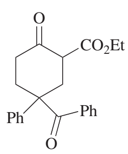
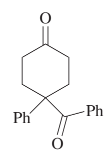
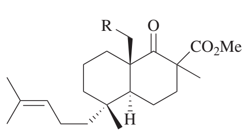
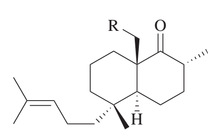
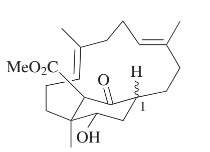
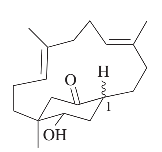
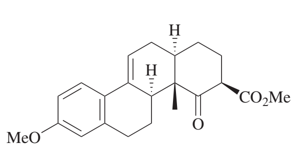
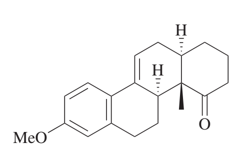
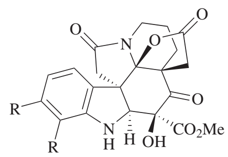
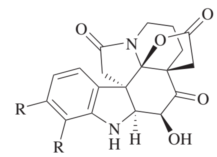
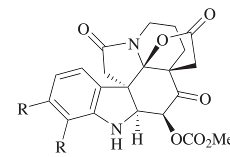
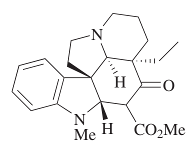
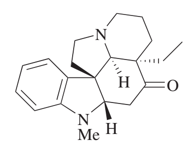
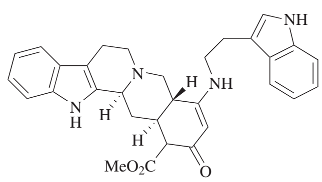
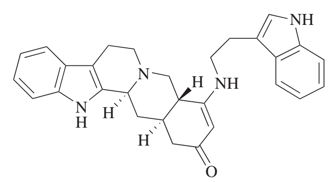
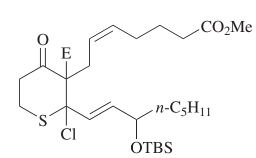
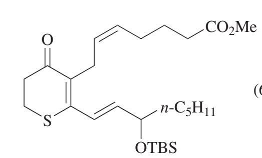
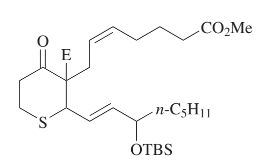
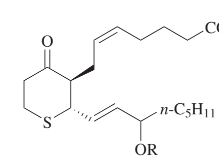
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	DMSO, $CaCl_2$•$2H_2O$, 150°, 14 h	 (37) +  (11)	71, 1695
	DMSO, $CaCl_2$•$2H_2O$, 150°, 14 h	 (—)	71, 1695
	DMSO, $CaCl_2$•$2H_2O$, 150°, 14 h	 (55)	71, 1695
C_{20}			
	Xylene, DABCO, reflux, 7 h	 (90)	1696
	HMPA, LiCl, 130°, 2 h	 R: H (72); MOMO (92)	H: 1697, 1698; MOMO: 1699, 61
	DMSO, H_2O, NaCl, reflux, 0.5 h	 C-1 Config.: α (90); β (90)	282
	DMSO, H_2O, NaCl, 150°, 4 h	 (90)[e]	1700

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	See table, reflux	 **I** +  **II**	265, 1701, 1327

R	Solvent	Additive(s)	Time (h)	I	II
H	MeCN	LiI or MgI_2	—	—	(77)
MeO	DMSO	H_2O, NaCl	—	(20)	—
MeO	MeCN	H_2O, MgI_2	4	(75)	"small amount"

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, LiCl, 150°, 25 min	 (—)	1702
C_{21} 	DMSO, NaCN, 107°, 40 h	 (58)	1703

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
 E = CO_2Me	DMF, LiI, reflux, 3 h	 (63)	124
 E = CO_2Me	DMF, H_2O, additives, LiI	 **I** R = TBS **II** R = H	124

Additives	Temp (°)	Time (h)	I	II
—	150–155	78	(40)	(43)
12-c-4, phosphate buffer (pH 7)	160	45	(69)	(19)

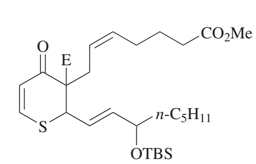
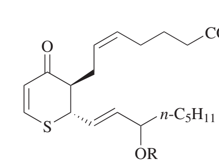
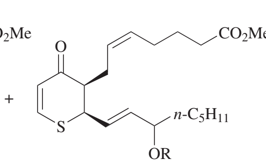
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
 E = CO_2Me	DMF, phosphate buffer, $MgCl_2$, pH 7, 160°, 21 h	 **Ia** R = TBS; **Ib** R = H +  **IIa** R = TBS; **IIb** R = H **Ia** + **IIa** (69), **Ib** + **IIb** (16), **Ia/IIa** = 3:2	125

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

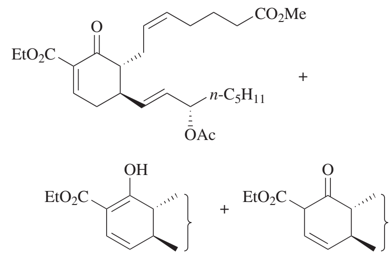
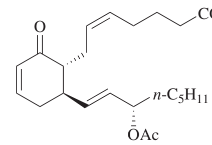
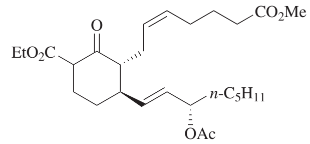
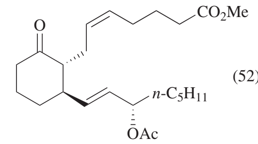
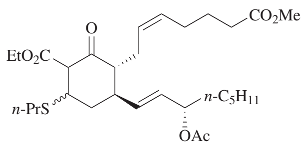
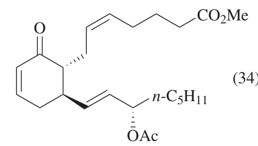
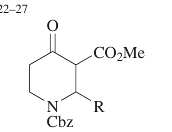
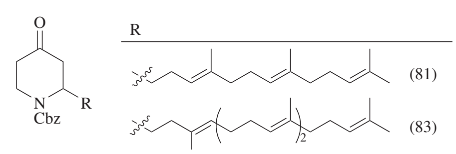
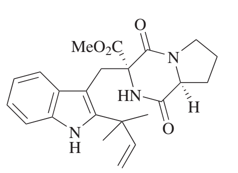
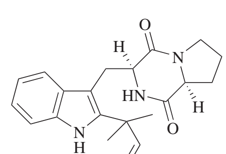
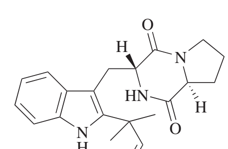
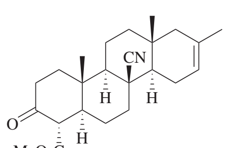
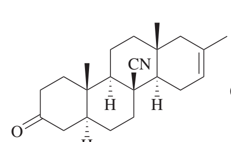
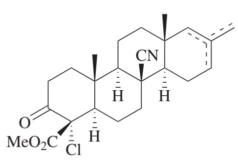
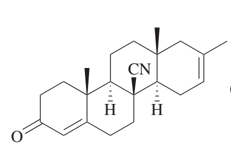
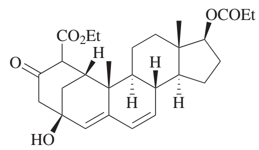
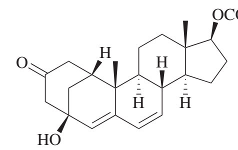
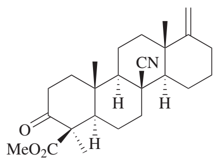
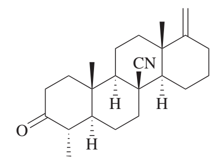
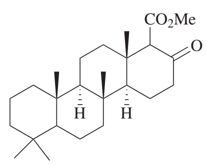
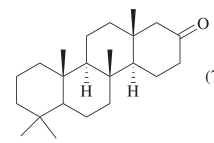
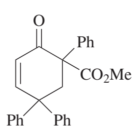
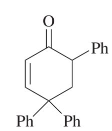
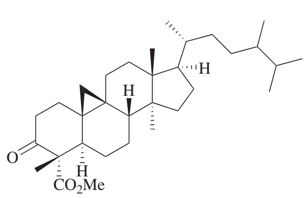
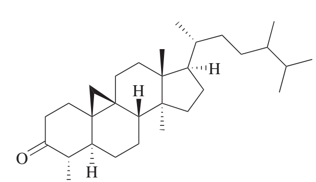
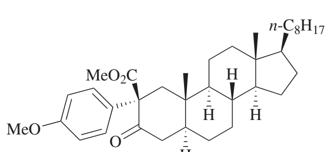
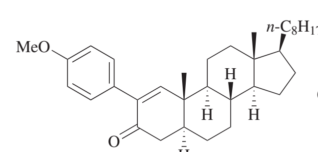
	β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}		DMSO, H_2O, NaCl, 150°, 4.5 h	 (40)	1704
		DMSO, H_2O, NaCl, 150°, 2 h	 (52)	1704
		DMSO, H_2O, NaCl, 150°, 2 h	 (34)	1704
$C_{22–27}$		DMSO, H_2O, NaCl, 100–120°, 6 h	 (81), (83)	1705
C_{22}		DMSO, $MgCl_2$•$6H_2O$, 130–140°, 2.5 h	 (59) +  (38)	1136
C_{23}		DMSO, H_2O, LiCl, 195–197°, 12 h	 (79)	1706
		DMSO, H_2O, LiCl, reflux, 12 h	 (28)	1706

TABLE 11B. DEALKOXYCARBONYLATIONS OF SIX-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

	β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23}		DMSO, H_2O, NaCl, 155–165°, 6 h	 (65)	1710
C_{24}		DMSO, H_2O, LiCl, reflux	 (65)	1708
		DMSO, H_2O, NaCl, reflux, 6 h	 (79)	1709
C_{25}		DMF, HOAc, NaI, reflux, 4.5 h	 (83)	1711
C_{31}		HMPA, NaCN, 75°, 3 h	 (80)	1712
C_{34}		DMSO, H_2O, NaCl, 180°, 24 h	 (33)	1713

[a] The substrate contained 35% of the methyl ester.

[b] The drawn product was the major isomer, and additional isomers were also observed.

[c] The product had a hydroxy group in the R^3 position.

[d] The product was isolated as the 2,4-dinitrophenylhydrazone derivative.

[e] The yield includes that of the preparation of the substrate.

[f] Decomposition was observed.

[g] The methyl ester in the R^1 position also underwent dealkoxycarbonylation under the reaction conditions.

[h] Starting material (24%) was also recovered.

[i] Starting material **II** was a single diastereomer. The product was obtained as a single isomer with unknown configuration at C-7 (in 35% yield) after chromatography.

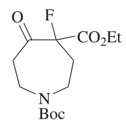
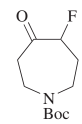
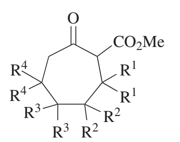
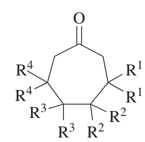
[j] The configurations of the two isomers could not be determined.

[k] The substrate contained 6% of the epimer in which all chiral centers except the one bearing the Ph_3SiCH_2 group are reversed.

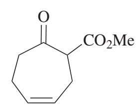
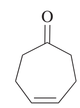
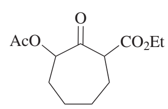
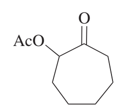
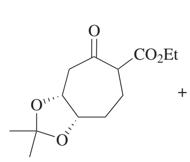
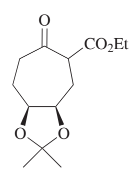
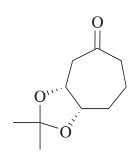
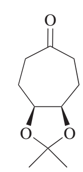
[l] The product partially cyclized under these conditions. Unreacted starting material was recovered after refluxing the substrate in HMPA in the presence of H_2O and NaI.

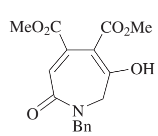
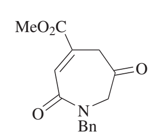
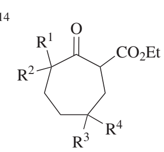
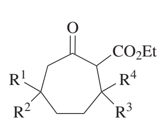
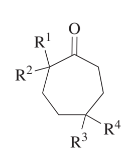
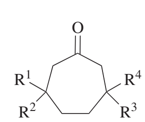
[m] The conditions used for Y = O gave an intractable gum.

TABLE 11C. DEALKOXYCARBONYLATIONS OF SEVEN-MEMBERED CYCLIC β-KETO ESTERS

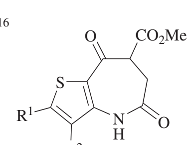
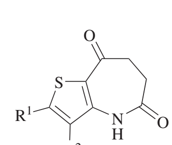
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	DMSO, H_2O, LiCl, 125°, 5 h	 (56)	1714
C_8 	DMSO, H_2O, 160°, 3 h	 (see below)	1715

R^1	R^2	R^3	R^4	
D	H	H	D	(75)
H	D	D	H	(85)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	2,6-Lutidine, $LiI•3H_2O$, 140°, 10 h	 (67)	1716
	DMSO, $CaCl_2•2H_2O$, 150°, 7 h	 (40)	1717
 + 	Krapcho	 +  (0)[a]	1718

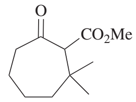
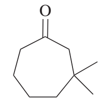
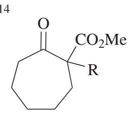
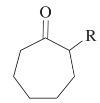
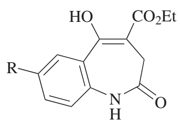
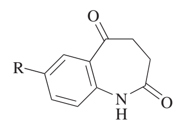
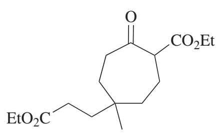
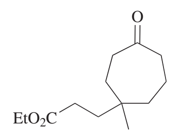
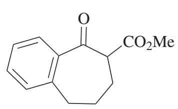
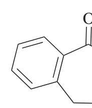
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, (salts), "heat"	 (0)[b]	1098
C_{9-14}  + 	H_2O, 230°, "several h"	 **I** +  **II** **I** + **II** (—)	1570

R^1	R^2	R^3	R^4	**I/II**
Me	H	H	H	82:18
Me	Me	H	H	88:12
Et	H	H	H	80:20
i-Pr	H	H	H	90:10
i-Pr	H	Me	H	67:33
i-Pr	H	H	Me	86:14
t-Bu	H	H	H	73:27
Ph	H	H	H	100:0

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-16} 	DMSO, H_2O	 (see below)	

R^1	R^2	Temp (°)	Time (h)		Refs.
H	H	150	1	(82)	1720
t-Bu	H	140	4–8	(40)	1721
4-$MeOC_6H_4$	H	140	4–8	(98)	1721
Ph	Me	140	4–8	(98)	1721

TABLE 11C. DEALKOXYCARBONYLATIONS OF SEVEN-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	2,4,6-Collidine, LiI	 (97)	1719
C_{10-14} 	DMSO, H_2O, LiCl, 180°, 1.5 h	 R: Et (81); n-C_5H_{11} (64); n-C_6H_{13} (81)	1722, 1723
C_{11} 	DMSO, H_2O, 150°	 R, Time (h): H, 1 (85); Br, 1 (90); I, 3 (71)	1720 (H), 1720 (Br), 1724 (I)
C_{12} 	DMSO, H_2O, NaCl, 165°, 6 h	 (85)	1725, 1726
	DMF, H_2O, HOAc, reflux, 5 h	 (78)	237

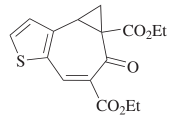
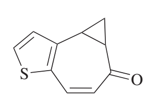
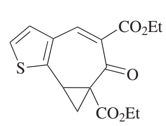
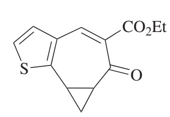
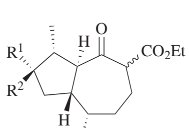
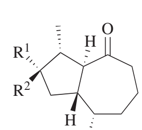
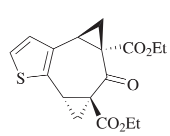
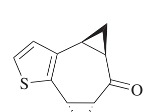
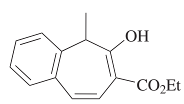
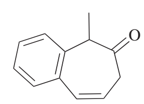
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, LiCl, reflux, 2 h	 (47)	1727
	DMSO, LiCl, reflux, 2 h	 (43)	1727
C_{13} 	DMSO, H_2O, NaCl, reflux, 4 h	 R^1, R^2, ^{c}: H, HO (89); H, TBSO (86); HO, H (93); TBSO, H (73); –O(CH_2)$_2$O– (93)	1728
	DMSO, LiCl, reflux, 2 h	 (61)	1727
	DMSO, H_2O, NaCl, 140°, 30 min	 (82)	1729

TABLE 11C. DEALKOXYCARBONYLATIONS OF SEVEN-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

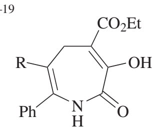
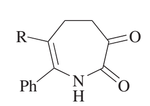
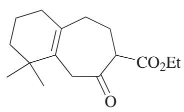
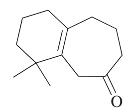
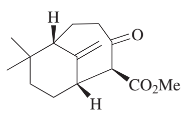
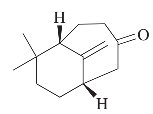
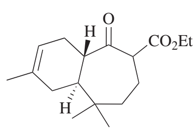
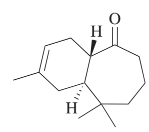
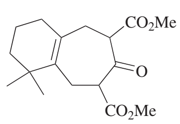
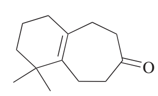
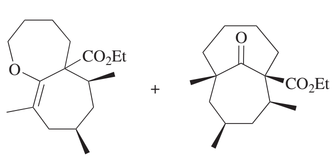
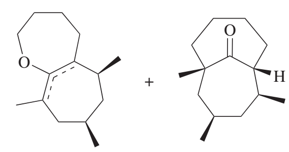
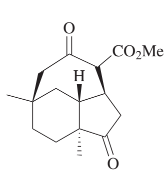
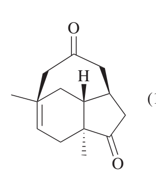
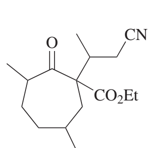
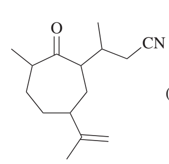
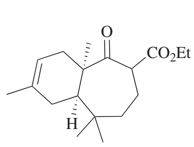
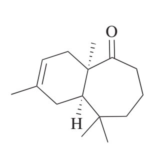
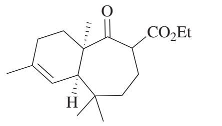
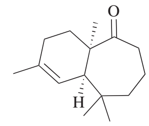
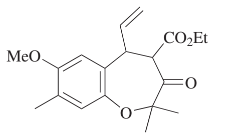
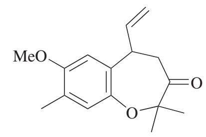
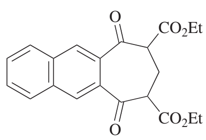
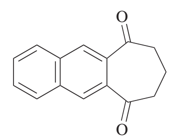
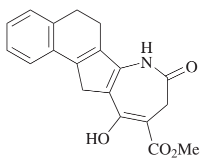
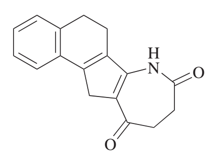
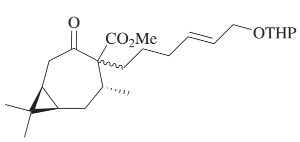
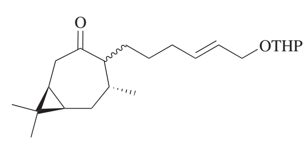
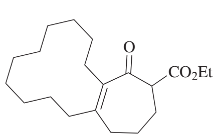
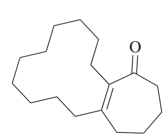
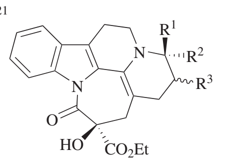
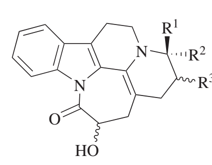
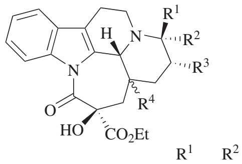
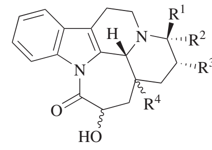
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-19} 	DMSO, $CaCl_2$, 140–150°, 15–60 min	 R: H (63); EtO (65); AcO (63); Ph (64)	1516
C_{14} 	DMSO, $CaCl_2$•$6H_2O$, 150°	 (—)	1612
	DMSO, H_2O, LiCl, 175°, 3 h	 (86)	1730
C_{15} 	2,4,6-Collidine, H_2O, LiI, reflux, 1 h	 (85)	1640
	DMSO, H_2O, NaCl, 128–135°, 4.5 h	 (73)	1731
 3:2	2,4,6-Collidine, LiI•$2H_2O$, reflux, 30 h	 I + II **I + II** (18), **I/II** = 3:2	1732
	DMSO, H_2O, NaCl, 160°, 3 h	 (100)	1733, 1734
C_{16} 	2,4,6-Collidine, LiI•$2H_2O$, reflux, 8 h	 (68)[c]	1735
	2,4,6-Collidine, H_2O, LiI, reflux, 2 h	 (86)	1736

TABLE 11C. DEALKOXYCARBONYLATIONS OF SEVEN-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

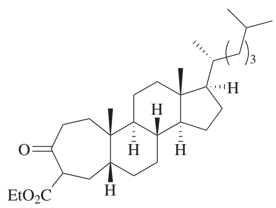
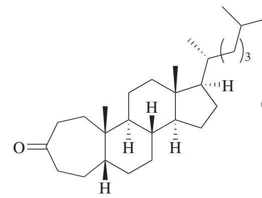
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	2,4,6-Collidine, H_2O, LiI, reflux, 45 min	 (10)	1736
	DMSO, H_2O, LiCl, 150–160°, 5 h	 (85)	1737
C_{17}			
	DMSO, H_2O, NaCl, 120°, 7 h	 (54)	1738
C_{18}			
	DMSO, H_2O, 140°, 4–8 h	 (98)	1721

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, LiI, reflux, 4 h	 (78)	1739
	DMF, H_2O, LiI, reflux	 (78)[c]	1590
$C_{19–21}$			
	MeCN, H_2O, MgI_2, reflux, 24 h		234
C_{21}			
	See table.		

R^1	R^2	R^3	Yield (%)
=O		H	(70)
H	H	Et	(77)

R^1	R^2	R^3	R^4	Config.	Cond.	Yield (%)	Refs.
H	H	H	Et	α	MeCN, MgI_2, *t*-BuOH, reflux, 24 h; then DMF, reflux, 48 h	(62)	1740, 234
=O		Et	H	β	MeCN, MgI_2, reflux, 24 h	(—)	234

TABLE 11C. DEALKOXYCARBONYLATIONS OF SEVEN-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

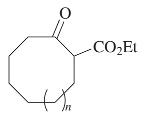
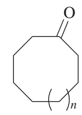
	β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29}		H_2O, 230°, 2.5 h	 (—)	1717

[a] The unidentified products had lost the isopropylidene protecting group and were highly polar. The same result was obtained with Al_2O_3 in dioxane, the sodium salt of 1,2-propanediol, or DMAP in toluene.

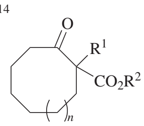
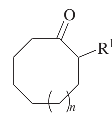
[b] Decomposition was observed.

[c] The yield includes that for the preparation of the substrate.

TABLE 11D. DEALKOXYCARBONYLATIONS OF EIGHT- AND HIGHER-MEMBERED CYCLIC β-KETO ESTERS

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{9–13}$ 	DMSO, H_2O		

n	Temp	Time (h)	Yield (%)	Refs.
1	reflux	3	(70)	15
2	150°	16	(83)	1741
5	reflux	4	(85)	15

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{10–14}$ 	See table.		

n	R[1]	R[2]	Solvent	Additive(s)	Temp	Time (h)	Yield (%)	Refs.
1	Me	Et	THF	$(n\text{-Bu})_4NF$	reflux	14	(69)	1742
1	$HOCH(Me)(CH_2)_2$	Et	THF	$(n\text{-Bu})_4NF$	reflux	3	(81)	1742
1	$n\text{-}C_5H_{11}$	Me	DMSO	H_2O, LiCl	180°	15	(78)	1722, 1723
2	n-Pr	Et	2,4,6-collidine	LiI	reflux	19	(60)	1743

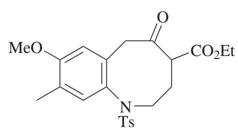
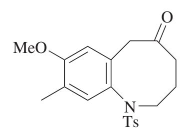
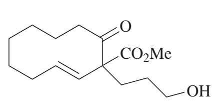
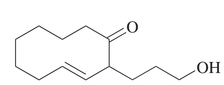
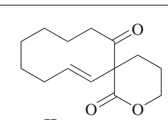
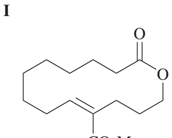
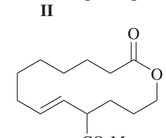
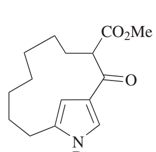
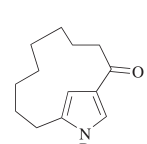
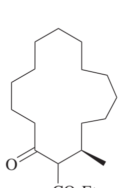
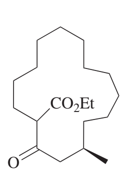
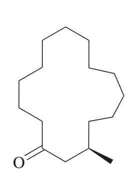
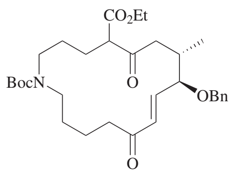
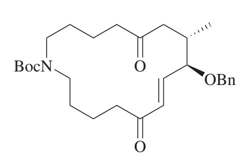
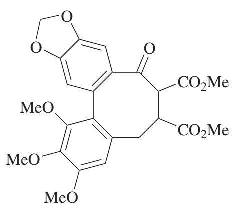
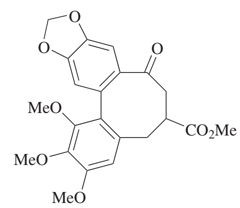
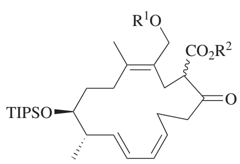
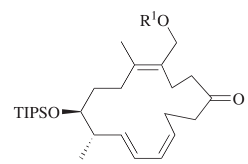
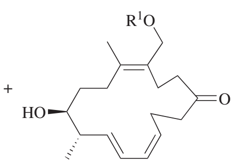
β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	DMF, H_2O, reflux, 5 h	 (100)	1744

TABLE 11D. DEALKOXYCARBONYLATIONS OF EIGHT- AND HIGHER-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	See table.	 **I** +  **II** +  **III** +  **IV**	1745

Solvent	Additive	Temp	Time (h)	I	II	III + IV	III/IV
THF	$(n\text{-Bu})_4NF$	rt; then reflux	1; 1.5	(61)	(0)	(20)	10:1
DMF	$(n\text{-Bu})_4NF$	rt	2	(19)	(57)	(16)	10:1
DMF	NaCl	reflux	6	(35)	(9)	(49)	7:3

β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 180–190°, 1.5 h	 (91)	1746
C_{17}  + 	DMSO, H_2O, 165°, 4 h	 (59)	194

		DMSO, H_2O, NaCl, 140°, 2 h	 (—)	1625
C_{18}		DMSO, H_2O, NaCl; or *o*-xylene, DABCO, reflux	 (0)	1747
C_{19}		See table.	 **I** +  **II**	

R^1	R^2	Solvent	Additive(s)	Temp (°)	Time (h)	I	II	Refs.
Me	*t*-Bu	2,4,6-collidine	LiI•$2H_2O$	100	15	(73)	(0)	287, 1748
PMB	Me	DMSO	H_2O, NaCN	125	6	(68)	(12)	288

TABLE 11D. DEALKOXYCARBONYLATIONS OF EIGHT- AND HIGHER-MEMBERED CYCLIC β-KETO ESTERS (*Continued*)

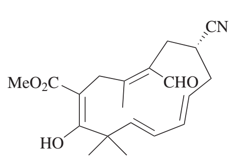
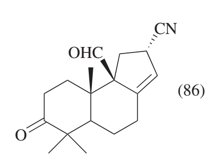
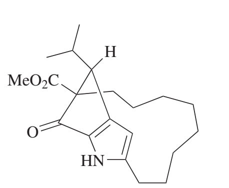
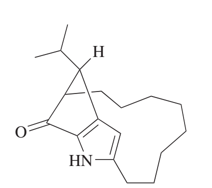
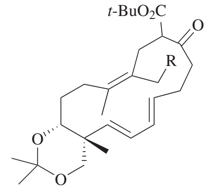
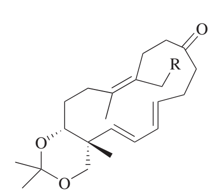
	β-Keto Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}		DMSO, H_2O, 155°, 3.5 h	 (86)	277
		DMSO, H_2O, NaCN, 140°	 (81)	1749
C_{20}	 R = $OSiPh_2$*t*-Bu	PhMe, Et_3N, 190°, 15 h	 (68)	1750

TABLE 12. DEALKOXYCARBONYLATIONS OF α-FORMYL ESTERS

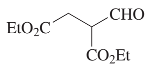
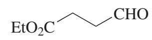
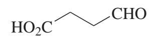
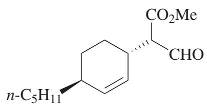
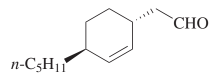
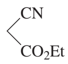
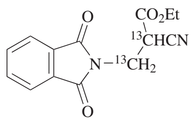
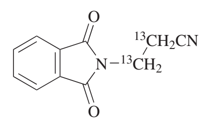
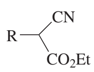
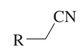
α-Formyl Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	H_2O, NaOAc, 130–140°, 1.5–2 h	 (78)	1751, 1752
	H_2O, 120–130°, 2 h	 (80)	1753
C_{14} 	DMF, H_2O, LiI, reflux, 1 h	 (89)	202

TABLE 13A. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED AND α-MONOSUBSTITUTED α-CYANO ESTERS

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	See table.	MeCN	

Solvent	Additive(s)	Temp (°)	Time (h)		Refs.
DMSO	H_2O, NaCl	135–165	2	(85–95)	333
DMSO	H_2O	150–142	2	(78–80)	116
—	H_2O	reflux	—	(—)	1754

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	DMSO, H_2O, NaCl	 (—)	1755
$C_{5–12}$ 	See table.		

R	Solvent(s)	Additive(s)	Temp (°)	Time (h)		Refs.
CH_2=CH	DMSO	H_2O, NaCl	160	4	(65)	1756
EtO_2CCH_2	DMSO	H_2O, NaCl	170–175	2.5	(76)	764
$EtO_2CCH_2CH_2$	DMSO	H_2O, LiCl	140	4	(92)	1757
n-Bu	DMSO	H_2O, NaCl	152–168	2	(85–95)	333
n-Bu	PhH, EtOH	KOH, 18-c-6	rt; then reflux	1; 48	(55)[a]	330
CH_2=CHC(Me)$_2$	DMSO	H_2O, NaCl	160	3	(82)	1758
Me_2C=$CHCH_2$	DMSO	H_2O, NaCl	160	3	(76)	1758
$Me_2CHCH_2CH_2$	DMSO	H_2O, NaCl	reflux	2	(52)[b]	1759
CH_2=CHCH(Me)CH(Me)	DMSO	H_2O, NaCl	150	1	(80)	415
Et_2CHCH_2	DMSO	H_2O, NaCl	170–180	8	(99)	1760
c-$C_5H_9CH_2CH_2$	DMSO	H_2O, NaCl	170–180	8	(86)	1760
$BzCH_2CH_2$	DMSO	H_2O, NaCl	reflux	20	(48)	1761

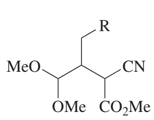
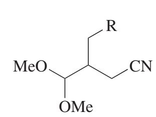
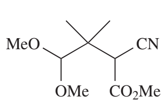
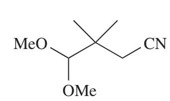
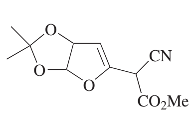
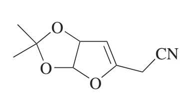
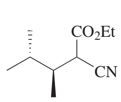
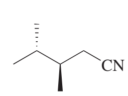
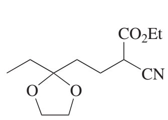
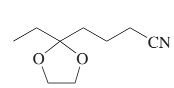
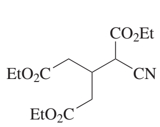
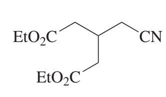
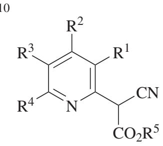
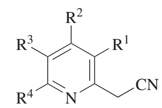
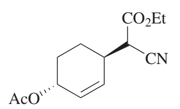
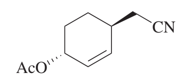
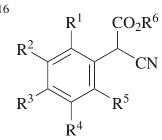
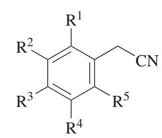
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	DMSO, H_2O, NaCl, 160°	 R: NC– (76); MeO_2C (80)	401
	DMF, LiI, reflux, 1.5–2 h	 (69)	341
	Krapcho	 (—)	477
C_8 	DMSO, H_2O, NaCl, 150°, 1 h	 (80)	1762
	DMSO, NaCl, 180°, 7 h	 (69)	1763
	DMSO, H_2O, LiCl, 140°, 4 h	 (75)	1764

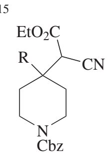
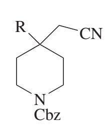
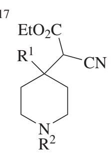
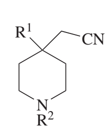
TABLE 13A. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED AND α-MONOSUBSTITUTED α-CYANO ESTERS (*Continued*)

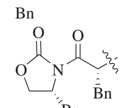
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-10} 	DMSO, H_2O, NaCl		

R^1	R^2	R^3	R^4	R^5	Temp (°)	Time (h)		Refs.
O_2N	H	H	H	Et	—	—	(0)[c]	1765
Cl	H	CF_3	H	Me	reflux	—	(—)	1766
NC	H_2N	NC	H_2N	Et	130–150	2.5	(67)	1767

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, H_2O, LiCl, 160°, 30 min	 (73)	1768
C_{9-16} 	DMSO, H_2O, additive		

R^1	R^2	R^3	R^4	R^5	R^6	Additive	Temp (°)	Time (h)		Refs.
H	H	H	H	O_2N	Et[d]	NaCl	140	6	"good"	1769, 1776
Cl	H	O_2N	H	Cl	Et	LiCl	165	0.5	(68)	1775
I	H	O_2N	H_2N	H	Et	LiCl	120	2.5	(—)	512a
H	H	H	Cl	NC	Me	—	reflux	6	(60)[b]	1770
H	H	Br	H	NC	Me	—	90	2	(81)[b]	1771
H	H	EtO_2C	H	H	Et	NaCl	—	—	(68)[b]	1772
H	Br	H	H	NC	Me	—[e]	115	1	(93)	1771
H	Me	H_2N	Me	H	Et	NaCl	140	3	(84)	1774
H	H	t-Bu(NC)$_2$C	H	H	Et	NaCl	130	—	(76)[b]	1773

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-15} 	DMSO, H_2O, LiCl, 160°	 (—) R = Me, Et, i-Pr, c-Pr, n-Bu, i-Bu, s-Bu, t-BuCH$_2$, c-C$_5$H$_9$, 4-tetrahydropyranyl, n-C$_6$H$_{13}$, 4-ClC$_6$H$_4$, or Bn	1777
C_{9-17} 	DMSO, H_2O, additive		

R^1	R^2	Additive	Temp (°)	Time (h)		Refs.
Me	Boc	LiCl	160	2.5	(86)	1778
EtO_2CCH_2	Bn	LiCl	200	2	(86)	1779
$EtO_2CCH(On$-Pr$)$	Bn	LiCl	200	—	(89)	1780
$EtO_2CCH(n$-Bu$)$	Bn	LiCl	200	—	(95)	1780
Bn	Cbz	NaCl	160	2	(97)	1781
	Bn	LiCl	134	0.5	(71)	1782

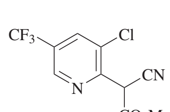
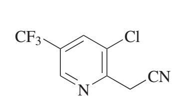
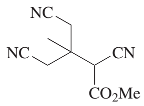
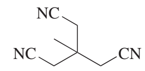
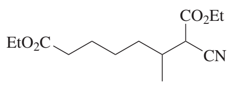
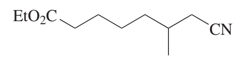
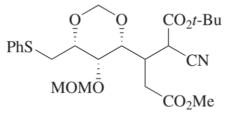
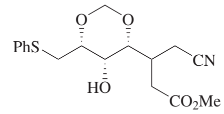
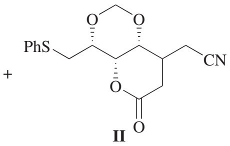
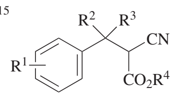
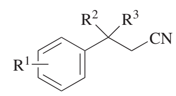
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, H_2O, NaCl, 160°	 (91)	1783

TABLE 13A. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED AND α-MONOSUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMF, 4-$H_2NC_6H_4SH$, Cs_2CO_3	 (72)	1785
C_{10} 	DMSO, NaCN, 160–170°, 6 h	 (68)	1784
	DMSO, H_2O, NaCl, 160°	 I +  II **I** + **II** (72–78), **I**/**II** = 1:1	238
C_{10-15} 	See table.		

R^1	R^2	R^3	R^4	Solvent	Additives	Temp	Time (h)		Refs.
H	H	H	Me	DMF	4-$H_2NC_6H_4SH$, Cs_2CO_3	85°	3	(86)	304
H	H	H	Et	DMF	4-$H_2NC_6H_4SH$, Cs_2CO_3	85°	10	(40)	304
2-I	H	H	Et	Krapcho	—	—	—	(94)	1786
2-MeO,4-Me	H	Me	Et	DMSO	H_2O, NaCl	160–180°	3	(84)	1787
H	H	$(MeO)_2CHCH_2$	Me	DMSO	H_2O, NaCl	150°	2	(81)	1789
H	H	$(MeO)_2CHCH_2$	Me	DMSO	H_2O, NaCl	Mw (850 W)	0.25	(81)	1789
4-F	H	MeO_2CCH_2	Et	DMSO	H_2O, NaCl	130°	24	(78)	1790
4-F	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(83)	1791
4-Cl	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(94)	1791
3-MeO	Me	Me	Et	DMSO	LiCl	130º	5	(75)	1792
4-MeO	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(74)	1791
3,5-$(MeO)_2$	Me	Me	Me	DMSO	H_2O, NaCl	reflux	5	(65)	1793
4-EtO	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(89)	1791
4-PhO	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(64)	1791
4-Me_2N	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(45)	1791
H	H	$AcCH_2$	Me	DMSO	H_2O	130º	40	(85)[b] (*R*)	1788
4-Me	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(86)	1791
4-CF_3	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(71)	1791
4-EtO	–$(CH_2)_4$–		Et	DMSO	H_2O, LiCl	reflux	4–5	(94)	1791
4-Et	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(97)	1791
4-*i*-Pr	Me	Me	Et	DMSO	H_2O, LiCl	reflux	4–5	(65)	1791

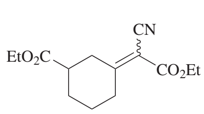
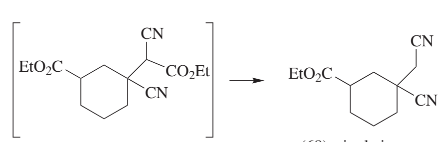
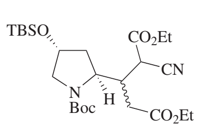
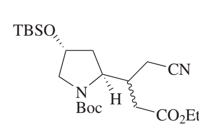
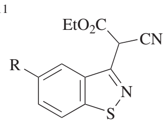
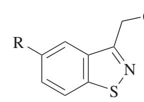
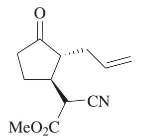
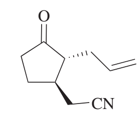
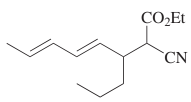
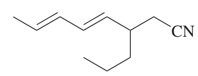
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	EtOH, H_2O, KCN	 (68) single isomer	1794
	DMSO, H_2O, NaCl, 140°, 1 h	 (67)	1795

TABLE 13A. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED AND α-MONOSUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)				Refs.
C_{10-11} 	DMSO, H_2O, 100°, 4–6 h	 (85–95)	R			
			H			1796, 1797
			Cl			1796
			O_2N			1796
			Me			1796
C_{11} 	DMSO, H_2O, 140–180°	 (80)				1798
C_{12} 	DMF, LiI, 150°, 4 h	 (65)				489

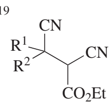
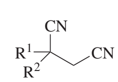
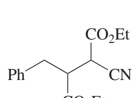
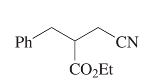
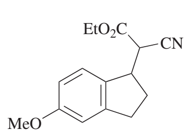
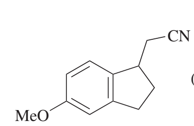
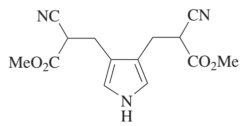
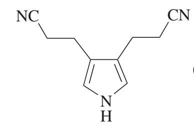
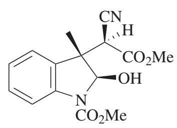
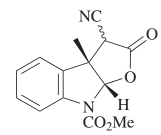
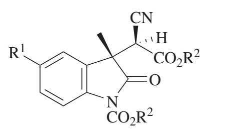
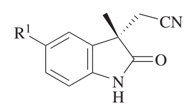
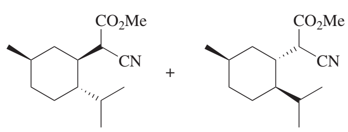
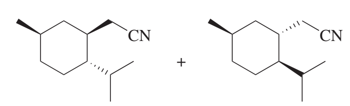
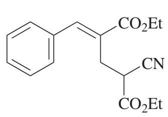
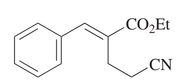
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	R^1	R^2		Refs.
C_{12-19} 	EtOH, H_2O, Na_2CO_3, KCN, reflux, 2–3 h		H	1-naphthyl	(50)	1799
			Me	n-C_6H_{13}	(60)	
			Me	Ph	(80)	
			Me	4-ClC_6H_4	(80)	
			Me	4-$H_2NC_6H_4$	(76)	
			Me	4-$O_2NC_6H_4$	(56)	
			Me	4-HOC_6H_4	(80)	
			Me	4-$MeOC_6H_4$	(84)	
			Me	4-MeC_6H_4	(85)	
			Me	Bn	(90)	
			Me	2-naphthyl	(70)	
			Et	Ph	(67)	
			Ph	Bn	(95)	
			Bn	Bn	(85)	
C_{12} 	DMSO, H_2O, NaCl, 140°, 2.5 h	 (77)				1800
	DMSO, LiCl, 180°, 5 h	 (72)				1801

TABLE 13A. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED AND α-MONOSUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	DMF, LiI, HOAc, 150°, 5 h	 (75)	1802
	DMSO, H_2O, NaCN, 100°, 30 min	 (70)	235
	DMSO, H_2O, NaCl, 160°	 R^1 / R^2: H / Me (88–93) MeO / Et (88)	1803, 1804 1803
C_{13} 	Krapcho	 (—)	1805
	*p*-Xylene, DMAP, reflux, 2 d	 (57)	299

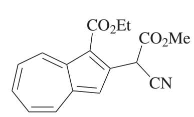
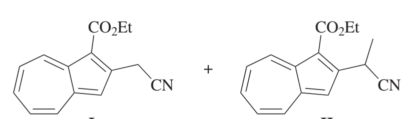
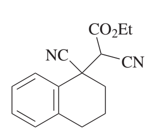
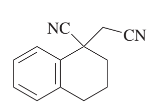
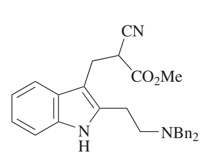
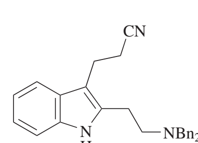
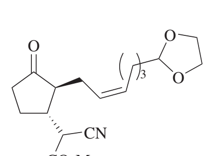
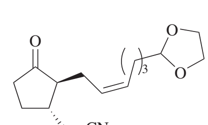
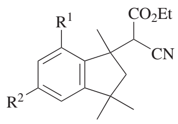
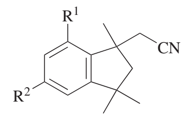
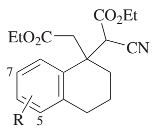
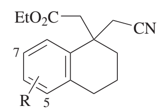
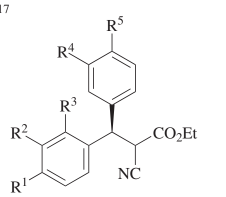
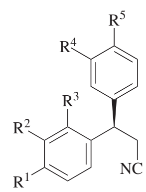
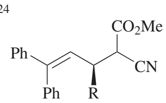
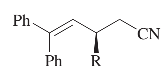
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	DMF, additive, LiI•$2H_2O$, 140°, 1 h	 I + II Additive / I + II / I/II: — / (—) / 1:1.6 HOAc / (75) / 100:0	24
	EtOH, H_2O, Na_2CO_3, KCN, reflux, 2–3 h	 (77)	1799
	DMF, H_2O, LiI	 (50)	1806
C_{15} 	DMSO, H_2O, NaCl, 175°, 2 h	 (79)	1807

TABLE 13A. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED AND α-MONOSUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	DMSO, additive, LiCl, 180°	 R[1] / R[2] / Additive / Time (h) H / MeO / — / — (60) MeO / H / H_2O / 5 (72)[b]	1808 1809
	DMSO, LiI, 170°, 0.5 h	 R 5-MeO (100) 6-MeO (83) 7-MeO (49)	1810
$C_{16–17}$			
	DMF, LiI, NaCN, 120°, 15 h		203

R[1]	R[2]	R[3]	R[4]	R[5]	Yield (%)	er
H	MeO	H	H	H	(81)	99.0:1.0
H	H	H	H	Br	(80)	99.0:1.0
H	H	MeO	H	H	(86)	99.5:0.5
H	H	Me	H	H	(70)	98.0:2.0
H	H	H	H	Me	(88)	98.5:1.5
Cl	H	H	H	Br	(89)	98.0:2.0
MeO	H	H	H	H	(95)	99.5:0.5
MeO	H	H	H	Br	(81)	99.0:1.0
MeO	H	H	H	Me	(91)	98.5:1.5
MeO	H	H	Me	H	(84)	98.0:2.0

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{19–24}$			
	DMSO, H_2O, NaCl, reflux, 4 h	 R / er Me 82.0:18.0 (74) Ph 95.0:5.0 (80)	1811

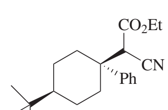
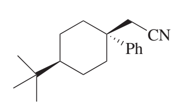
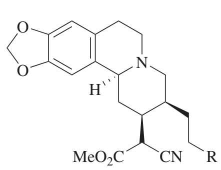
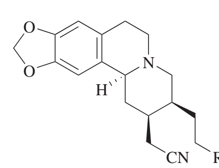
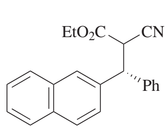
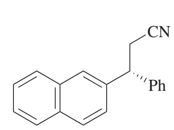
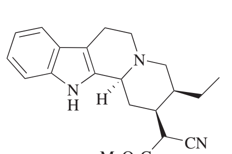
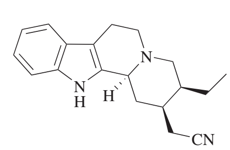
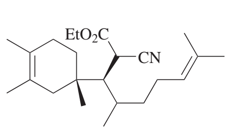
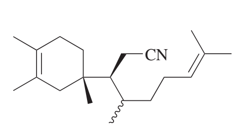
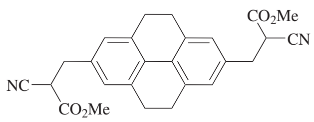
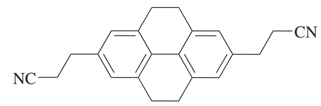
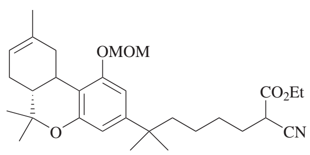
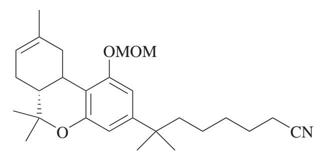
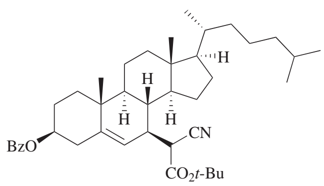
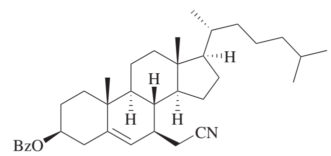
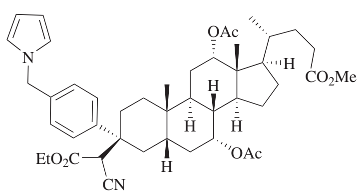
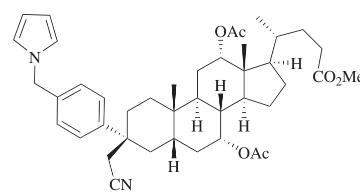
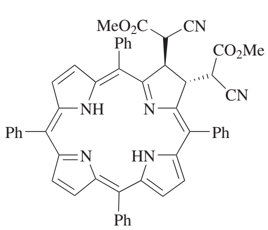
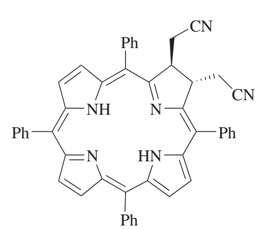
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	DMSO, H_2O, NaCl, 160°, 2 h	 (90)	1812
	DMSO, H_2O	 R / Temp / Time (h) NC / reflux / 2–3 (75–80) NC[f] / 170° / — (96)[b] EtO_2C / reflux / 2–3 (75–80)	1813 1814 1813
C_{20}			
	DMF, LiI, NaCN, 120°, 15 h	 (94) 99.0:1.0 er	203
	DMSO, NaCN, 145°, 1.5 h	 (89)	1815
C_{21}			
	DMSO, H_2O, NaCl, 150°, 1 h	 (84)	706

TABLE 13A. DEALKOXYCARBONYLATIONS OF α-UNSUBSTITUTED AND α-MONOSUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24} 	DMSO, H_2O, HOAc, NaCl, 150°, 3 h	 (52)	1816
C_{26} 	DMSO, H_2O, 140°, 16 h	 (54)	1817
C_{30} 	DMSO, H_2O, LiCl, 140°, 20 h	 (84)	1818
C_{34} 	DMSO, H_2O, NaCl, 150°, 4 h	 (85)	1819
C_{50} 	DMSO, H_2O, NaCl, 140°, 14 h	 (100)	206

[a] 2-Cyanohexanoic acid was formed in 21% yield.

[b] The yield includes that of the preparation of the substrate.

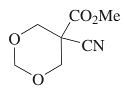
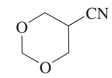
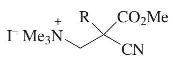
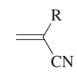
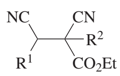
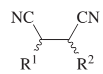
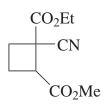
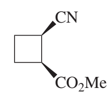
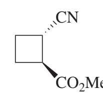
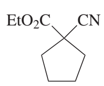
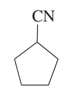
[c] The reaction also failed with NaCN in DMSO or LiI in DMF. The corresponding *tert*-butyl ester could be dealkoxycarbonylated thermally in the presence of a catalytic amount of *p*-TsOH.

[d] The substrate and product had ^{14}C in the cyano group.

[e] Addition of LiCl, NaCl, or NaCN gave multiple products.

[f] The cyano group α to the carbomethoxy group contained ^{14}C.

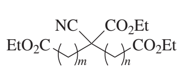
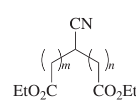
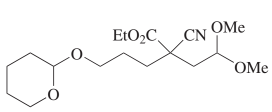
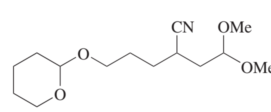
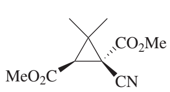
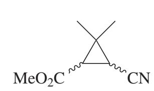
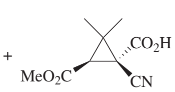
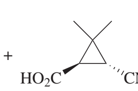
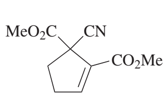
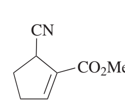
TABLE 13B. DEALKOXYCARBONYLATIONS OF α,α-DISUBSTITUTED α-CYANO ESTERS

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	Krapcho	 (—)	1820
C_{6-11} 	DMF, 80°, 48 h	 (see table below)	205
C_{7-15} 	DMSO, H_2O, KCN, 145°, 7 h	 (see table below)	26
C_7 	DMSO, H_2O, NaCl, 150°, 4 h	 I +  II; **I + II** (77), **I/II** = —	1821, 1822
	DMSO, additive(s)	 (see table below)	1823

R	
Et	(41)
allyl	(66)
i-Pr	(41)
n-C_6H_{13}	(68)
Bn	(71)

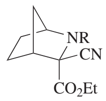
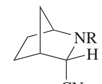
R^1	R^2	[a]	Config.
Me	Me	(23)	*meso* + *racemic*
Et	Et	(62)	*meso* + *racemic*
i-Pr	H	(70)	—
i-Pr	*i*-Pr	(61)	*racemic*
i-Pr	Bn	(53)	*threo*
Ph	Me	(17)	*threo* + *erythro*

Additive(s)	Temp	Time (h)	
NaCN	reflux	2	(75)
H_2O, NaCl	—	—	(0)

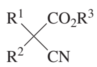
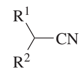
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-9} 	DMSO	 (see table below)	764
C_8 	DMSO, KOAc, 160°, 17 h	 (87)	1824
	See table.	 I +  II +  III	29
	DMF, LiI, reflux	 (67)	1825

m	*n*	Additive	Temp (°)	Time (h)	
1	1	NaCl	160–165	4	(83)
1	2	NaCl	175–180	2	(81)
1	2	KCl	180–185	1.5	(92)
2	2	NaCl	185–190	5.5	(77)

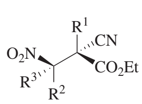
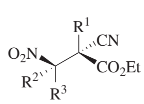
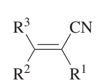
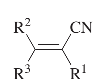
Conditions	I	*cis*/*trans*	II	III
DMSO, H_2O (2 eq), LiCl (2 eq), $NaHCO_3$, 165°, 0.5 h	(89)	2:1	(—)	(—)
DMSO, H_2O (7 eq), LiCl (7 eq),[b] $NaHCO_3$, 165°, 0.5 h	(64)	5:1	(20)	(—)
$HO(CH_2)_3OH$, H_2O, $NaHCO_3$, reflux	(—)	—	(—)	"only product"

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	See table.	 I +  II	1826

R	Solvent	Additive(s)	Temp (°)	Time (h)	I + II	I/II
H	DMF or HMPA	H_2O and/or NaCl or NaI or NaCN	150	—	(0)	—
H	DMF	$CaCl_2$•$2H_2O$	160	—	(0)	—
CF_3CO	DMF or HMPA	H_2O and/or NaCl or NaI, or NaCN	150	—	(0)	—
CF_3CO	DMF	$CaCl_2$•$2H_2O$	160	2.5	(79)	60:40[c]

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-17} 	See table.		

R^1	R^2	R^3	Solvent	Additive(s)	Temp (°)	Time		Refs.
Et	C_6F_5	Et	DMSO	H_2O	160	5 d	(78)	1827
i-Pr	*i*-Pr	Et	1-oxo-1-methylphospholine	H_2O, NaCl	160–170	9 h	(85)	113
CH_2=$CHCH_2$	CH_2=$C(Me)CH_2CH_2$	Me	DMSO	H_2O, NaCl	reflux	12 h	(85)	1828
CH_2=$C(Me)CH_2$	CH_2=$C(Me)CH_2$	Et	DMSO	NaCl	150	7.5 h	(78)	1829
Bn	2-$BrC_6H_4CH_2$	Me	DMSO	H_2O, LiCl	132	0.75 h	(48)	1830

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-18}  I +  II	HMPA, NaBr, 120°, 1.5 h	 III +  IV	

R^1	R^2	R^3	I/II	III + IV	III/IV	Refs.
i-Pr	Me	Me	—	(70)[a]	—	233, 1831
i-Pr	Me	Et	—	(62)[a]	43:57	1831
i-Pr	–$(CH_2)_5$–		—	(63)[a]	—	1831
i-Pr	Me	Bn	62:38	(—)	61:39	233
n-Bu	Me	Me	—	(72)[a]	—	1831
Bn	Me	Me	—	(75)[a]	—	1831
Bn	Me	Et	57:43	(75)[a]	55:45	233, 1831
Bn	Me	*n*-Pr	53:47	(—)	53:47	233
Bn	Me	*n*-Bu	55:45	(—)	54:46	233
Bn	Me	*n*-C_6H_{13}	51:49	(—)	52:48	233
Bn	–$(CH_2)_5$–		—	(70)[a]	—	1831
n-C_8H_{17}	Me	Me	—	(72)[a]	—	1831

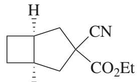
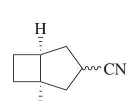
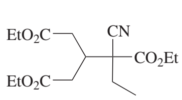
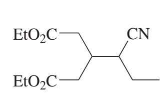
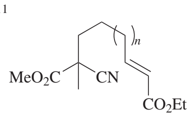
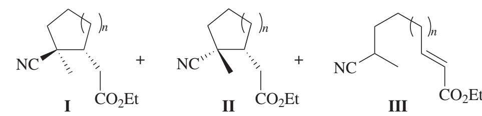
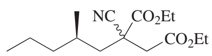
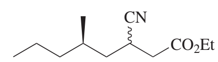
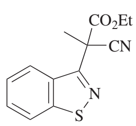
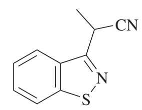
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, H_2O, LiCl, 150°, 22 h	 (44) 3:2 dr	1832, 1833
C_{10} 	DMSO, H_2O, LiCl, 140°, 4 h	 (74)	1764

TABLE 13B. DEALKOXYCARBONYLATIONS OF α,α-DISUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11}			
	HMPA, LiCl, 120°, 4 h		225
C_{11}			
	See table.		125a
	DMSO, H_2O, 100°, 4–6 h	 (—)	1797

n	**I + II + III**	**I/II/III**
1	(67)	77:23:0
2	(45)	69:15:16

Solvent	Additive(s)	Temp (°)	Time (h)		Purity (%)
DMSO	H_2O, NaCl	135	120	(85)	72
DMSO	H_2O, NaCl, $(n\text{-Bu})_4NBr$	135	36	(93)	80
DMSO	H_2O, LiCl	100	28.5	(85)	97
NMP	LiCl	100	48	(89)	—
DMF	LiCl	100	48	(46)	—
DMSO	LiCl	100	48	(34)	—
DMSO	$CaCl_2$	100	48	(55)	—
H_2O	LiCl	100	48	(0)	—

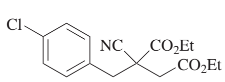
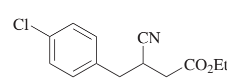
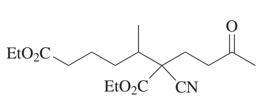
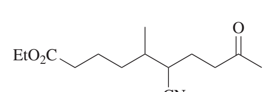
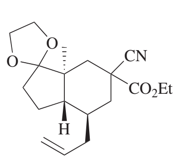
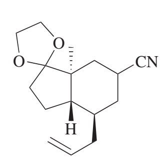
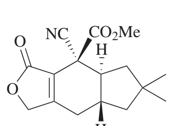
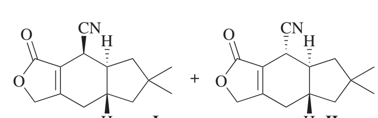
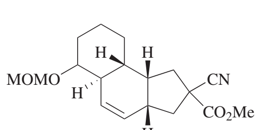
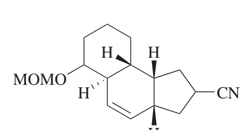
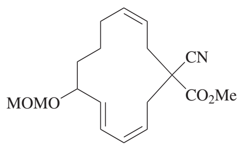
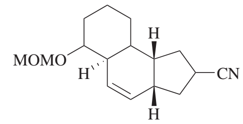
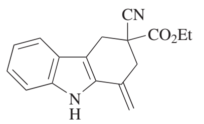
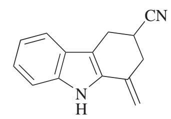
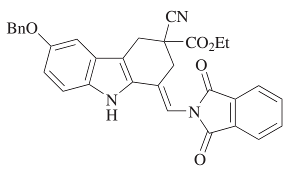
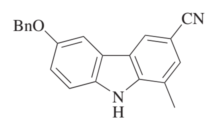
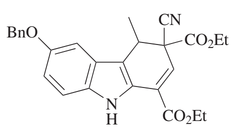
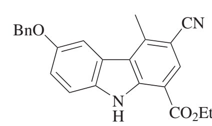
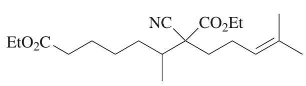
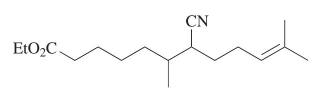
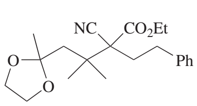
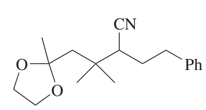
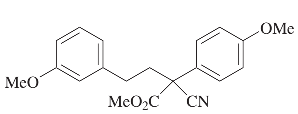
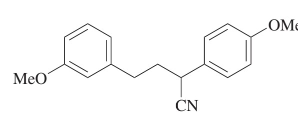
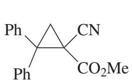
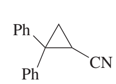
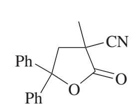
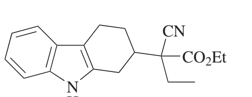
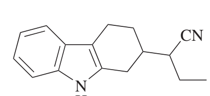
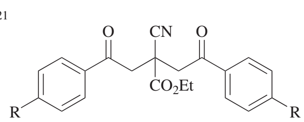
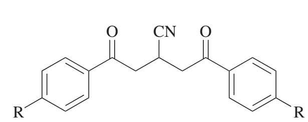
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	DMSO, H_2O, NaCl, 180°, 2 h	 (71)	1834
C_{13}			
	DMSO, H_2O, NaCl, reflux, 6 h	 (86)	1835
C_{15}			
	DMF, LiI, 140°, 40 h	 (—) (85)	1836
	DMF, NaCN, 160°, 4 h	 **I + II** (63), **I/II** = 2:1	63
	DMSO, NaCN, 160°, 8 h	 (97)	204

TABLE 13B. DEALKOXYCARBONYLATIONS OF α,α-DISUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	DMSO, NaCN, 160°, 8 h	 (89)	204
	DMSO, H_2O, LiCl	 (84)	1837
	See table.	 Cond.: DMSO, H_2O, LiCl (0)[d]; HMPA, KCN, 125°, 48 h (12)	1838
C_{16}			
	DMSO, H_2O, LiCl, 100°, 26 h	 (45)	1838
	DMSO, NaCN, 160–170°, 6 h	 (75)	1784

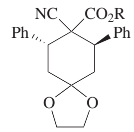
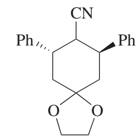
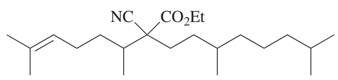
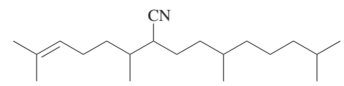
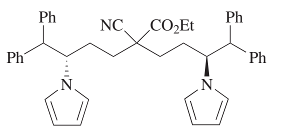
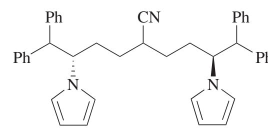
α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	HMPA, LiCl, 160°, 3 h	 (85)	1839
	DMSO, NaCN, reflux	 (91)	1840, 1841
	DMF, LiBr	 **I** +  **II**	1842, 1843
	DMSO, H_2O, NaCl, 160°, 18 h	 (68)	1844
C_{19-21}			
	DMSO, H_2O, NaCl, 130–150°, 2.5 h	 R = H (67); Cl (66); Me (68)	887

Cond.	
DMSO, H_2O, LiCl	(0)[d]
HMPA, KCN, 125°, 48 h	(12)

Temp (°)	Time (h)	I	II
126 (sealed tube)[e]	24	(53)	(23)
120 (open flask)	20	(—)	(0)

R	
H	(67)
Cl	(66)
Me	(68)

TABLE 13B. DEALKOXYCARBONYLATIONS OF α,α-DISUBSTITUTED α-CYANO ESTERS (*Continued*)

α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	DMSO, H_2O, NaCl	 R / Temp (°) / Time (h): Me / 173 / 4 / (88); Et / 147–170 / 4.5 / (78)	1845
C_{21} 	DMSO, KOAc, 150°, 4 h	 (90)	1846
C_{43} 	DMSO, NaCN, 160°, 6 h	 (72)	1847

[a] The yield includes that of the preparation of the substrate.

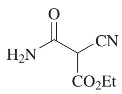
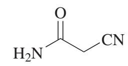
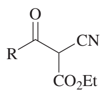
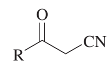
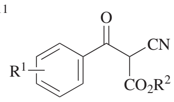
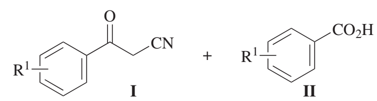
[b] The rate of dealkoxycarbonylation was diminished under these conditions. Addition of weak acids such as boric acid resulted in partial cyclopropane ring opening.

[c] The *endo*/*exo* ratio remained at 60:40 on equilibration under unspecified conditions.

[d] No reaction was observed.

[e] The methyl bromide that could not escape caused formation of product **II**.

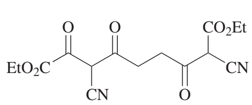
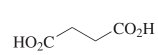
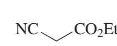
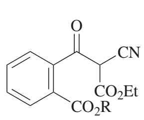
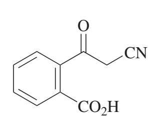
TABLE 14. DEALKOXYCARBONYLATIONS OF α-ACYL α-CYANO ESTERS

α-Acyl α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	H_2O, reflux, 5 h	 (49)	1094
C_{6-9} 	DMSO, H_2O, 120°		
C_{10-11} 	See table.	 I + II	

R	Time (h)		Refs.
Et	—	(85)	1848, 1849
n-Pr	1	(—)	1849
i-Pr	1	(—)	1849
n-Bu	1	(—)	1849
n-C_5H_{11}	1	(—)	1849

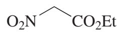
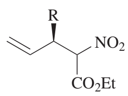
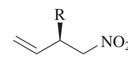
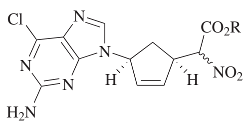
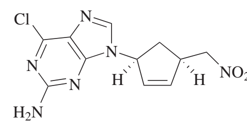
R^1	R^2	Solvent	Additives	Temp	Time (h)	I	II	Refs.
H	Me	H_2O	—	reflux	"several"	(—)	(—)	1850, 1851
H	Et	H_2O	—	"heat"	—	(32)	(55)	1852
3-Cl	Et	H_2O	—	"heat"	—	(21)	(48)	1852
4-Cl	Me	H_2O	—	"heat"	—	(45)	(32)	1852
2,5-Cl_2	Et	H_2O	—	"heat"	—	(0)[a]	(0)[a]	1852
4-H_2N	Me	H_2O	—	"heat"	—	(81)	(0)	1852
2-O_2N	Et	H_2O	—	"heat"	—	(44)	(18)	1852
3-O_2N	Et	H_2O	—	"heat"	—	(23)	(26)	1852
4-O_2N	Et	H_2O	—	"heat"	—	(0)	(100)	1852
4-MeO	Me	H_2O	—	"heat"	—	(93)	(0)	1852
4-PhO	Me	DMSO	H_2O, NaCl	—	—	(92)	(0)	207
2-Me	Et	H_2O	—	reflux	—	(—)	(0)	1853

TABLE 14. DEALKOXYCARBONYLATIONS OF α-ACYL α-CYANO ESTERS (*Continued*)

α-Acyl α-Cyano Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	H_2O	 (—) +  (—)	1754
	H_2O, reflux, "several h"	 (—) R: Me, Et, *n*-Bu	1754

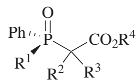
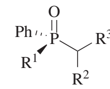
[a] No reaction was observed.

TABLE 15. DEALKOXYCARBONYLATIONS OF α-NITRO ESTERS

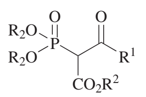
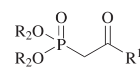
α-Nitro Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 	PhH, EtOH, KOH, 18-c-6, rt, 2 h; then reflux, 24 h	$MeNO_2$ (0)	330
C_{8-13} 	DMF, H_2O, LiI, 2-*t*-butylhydroquinone, 150°, 5 h	 R | | er *n*-Pr | (95) | >99.5:0.5 Ph | (70) | >99.5:0.5 $Ph(CH_2)_2$ | (75) | >99.5:0.5	126
C_{12} 	See table.		1854

R	Solvent	Additive(s)	Temp (º)	Time (h)	
Et	DMSO	H_2O, NaCl	150	4	(66)
$TMSCH_2CH_2$	MeCN	CsF	50	24	(62)

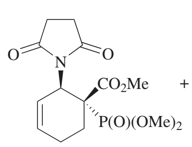
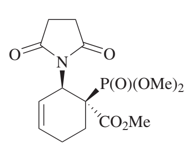
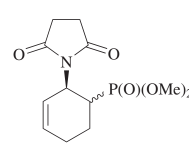
TABLE 16. DEALKOXYCARBONYLATIONS OF α-PHOSPHORYL ESTERS AND PHOSPHONATES

α-Phosphoryl Ester or Phosphonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-9} 	DMSO, H_2O, LiCl		

R^1	R^2	R^3	R^4	Temp (°)	Time (h)		Refs.
Me	Me	Me	Me	180	6–18	(14)	208, 1855
Et	H	H	Me	180	6–18	(34)	208, 1855
Et	H	H	(–)-menthyl	reflux	12	(60)	209, 103
Et	CD_3	H	(–)-menthyl	180	6–18	(62)	103
Et	Me	Me	(–)-menthyl	180	6–18	(9)	103
Et	Et	H	(–)-menthyl	180	6–18	(50)	103
Et	CH_2=CH	H	(–)-menthyl	180	2	(60)	103
Et	CH_2=$CHCH_2$	H	(–)-menthyl	180	6–18	(70)	103
Et	Bn	H	(–)-menthyl	180	6–18	(67)	103
Bn	H	H	Me	180	6–18	(21)	208, 1855

α-Phosphoryl Ester or Phosphonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-9} 	H_2O, 120–140°, 2–3 h		1856

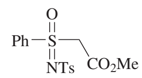
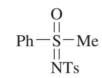
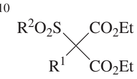
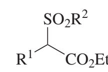
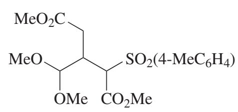
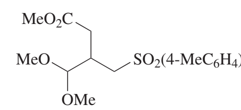
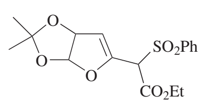
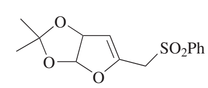
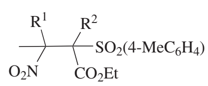
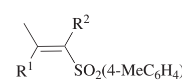
R^1	R^2	[a]
Me	Me	(70)
Me	Et	(82)
Et	Et	(98)
2-furyl	Et	(64)
n-C_5H_{11}	Et	(70)
Ph	Et	(75)
4-ClC_6H_4	Et	(75)
2-$O_2NC_6H_4$	Et	(79)
$PhthNCH_2$	Et	(84)
PhthNCH(i-Bu)	Et	(90)

α-Phosphoryl Ester or Phosphonate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7  + 	DMSO, H_2O, LiCl, reflux	 (0)[b]	1857

[a] The yield is for the three-step procedure starting with the alkyl 2-(dimethoxyphosphoryl)acetate.

[b] Slow monodemethylation of the phosphonate was observed.

TABLE 17. DEALKOXYCARBONYLATIONS OF α-SULFONYL AND α-SULFOXIMINO ESTERS

α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2  (*R*) or (*S*)	DMSO, NaCN, 120°	 (—) no racemization	211
C_{4-10} 	DMSO, Triton B, rt, 1 h	 R^1 R^2 Me Me (56) Et Me (68) Ph Me (72) Ph Ph (73) Bn Me (72)	328
C_6 	DMSO, H_2O, NaCl, 160°	 (80)	401
	Krapcho	 (—)	477
C_{6-7} 	HMPA, NaBr, 130–140°	 R^1 R^2 Time (h) Me Me 2 (87) Me Et 3 (79) Et Me 3 (71)	233

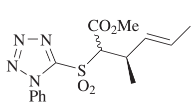
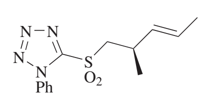
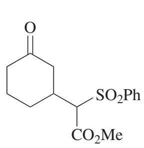
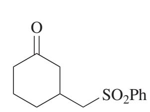
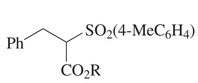
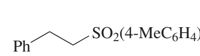
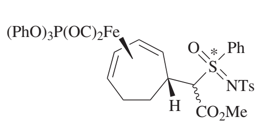
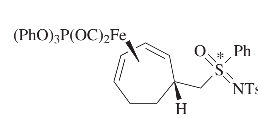
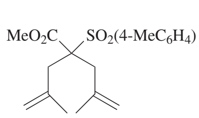
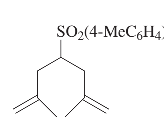
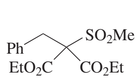
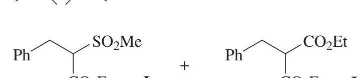
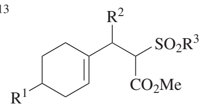
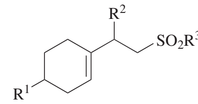
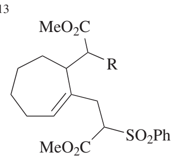
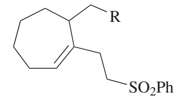
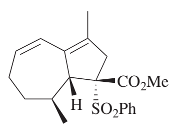
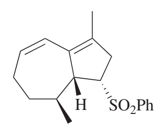
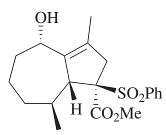
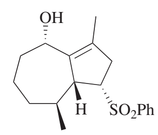
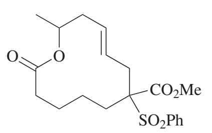
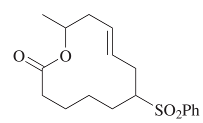
α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7  1:1 mixture	DMSO, NaCl, 150°, 4 h	 (64)	1858, 1859
C_8 	DMSO, H_2O, NaCl, reflux, 8 h	 (63)	1860
C_9 	DMF, 4-$H_2NC_6H_4SH$, Cs_2CO_3, 85°	 R Time (h) Me 2 (94) Et 3 (0)	304
	DMSO, NaCN, 80°, 48 h	 (80)	211
C_{10} 	DMSO, H_2O, NaCl, 170°, 18 h	 (99)	1861
	PhH, DABCO, reflux, 8 h	 **I** + **II** (—), **I**/**II** = 52:48	837

TABLE 17. DEALKOXYCARBONYLATIONS OF α-SULFONYL AND α-SULFOXIMINO ESTERS (*Continued*)

α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-13} 	DMF, LiI•3H_2O, NaCN, 120°, 12 h	 R^1 / R^2 / R^3: H / Me / Ph (100) *t*-Bu / H / Me (86)	541
C_{12-13} 	DMF, LiI, NaCN, 130°, 24 h	 R: PhO_2S (71) MeO_2C (52)	88
C_{13} 	DMF, NaI, $NaHCO_3$, 145°, 3 h	 (81)[a]	210
	DMF, NaI, 150°	 (83)[a]	210
	HMPA, $Me_4N^+AcO^-$, 95–100°, 3 h	 (86)	1862, 1863

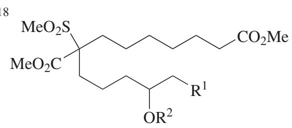
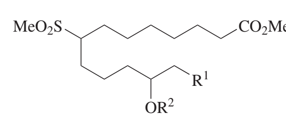
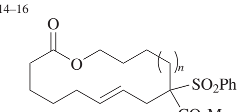
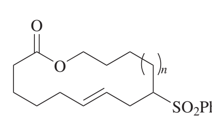
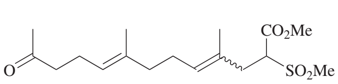
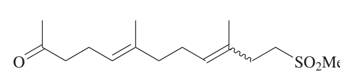
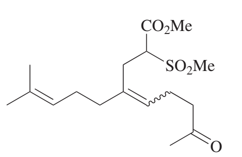
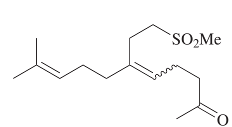
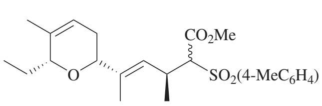
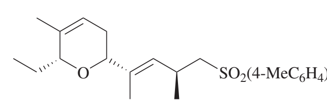
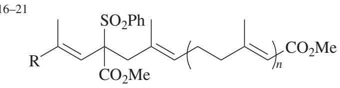
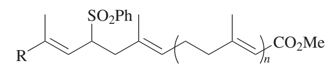
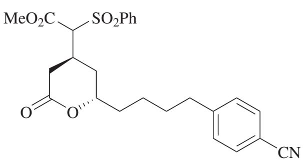
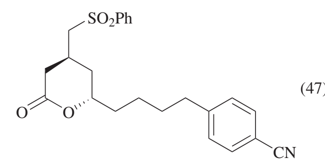
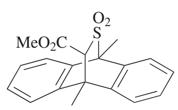
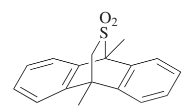
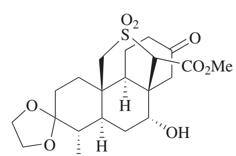
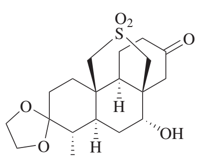
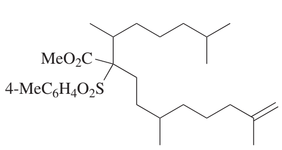
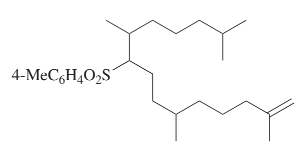
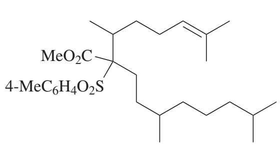
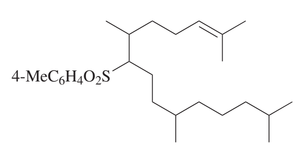
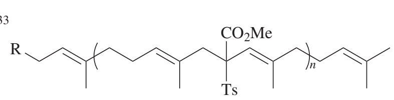
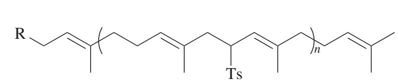
α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14-18} 	DMSO, H_2O, NaCl, 185°, 5 h	 R^1 / R^2: 4-FC_6H_4O / Bz (98) *n*-Bu / Ac (95)	1864
C_{14-16} 	HMPA, $Me_4N^+AcO^-$	 *n* / Temp (°) / Time (h): 1 / 90–95 / 6 (76) 3 / 90 / 11 (82)	1862
C_{15} 	DMF, LiI•3H_2O, NaCN, 130°	 (78)	1865
	DMF, LiI•3H_2O, NaCN	 (78)	1866
	HMPA, $Me_4N^+AcO^-$, 100°, 17 h	 (71)	1867

TABLE 17. DEALKOXYCARBONYLATIONS OF α-SULFONYL AND α-SULFOXIMINO ESTERS (*Continued*)

α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16-21} 	DMF, additives		

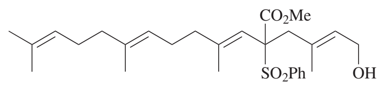
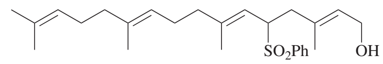
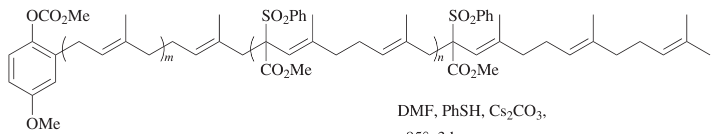
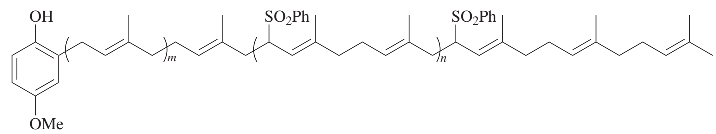
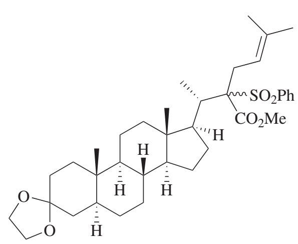
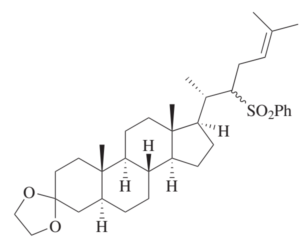
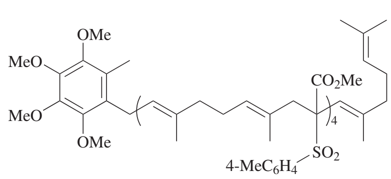
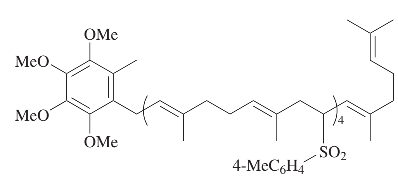
R	n	Additives	Temp (º)	Time (h)		Refs.
Me	1	LiI•3H_2O, NaCN	120	17	(59)	623
CD_3	1	4-$H_2NC_6H_4SH$, Cs_2CO_3	85	1.5	(88)	1868
CD_3	1	LiI•3H_2O, NaCN	—	—	(44)	1868
Me	2	LiI•3H_2O, NaCN	120	17	(44)	623, 541
CD_3	2	4-$H_2NC_6H_4SH$, Cs_2CO_3	85	1.5	(64)	1868

α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	DMSO, H_2O, NaCl, 160°, 1.5 h; then 180°, 0.5 h	 (47)	1869
	DMSO, H_2O, NaCl, 160°, 6 h	 (86)	1870
	HMPA, $Me_4N^+AcO^-$, 125°, 2 h	 (35)	1871

α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	DMSO, KOAc, 150–160°, 7 h	 (90)	1873
	DMSO, H_2O, NaCl, 150–160°, 5 h	 (91)	1874
C_{21-33} 	See table.		304, 1875

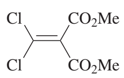
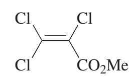
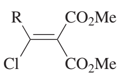
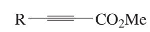
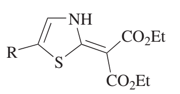
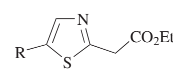
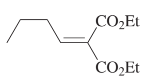
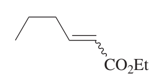
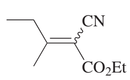
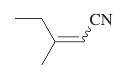
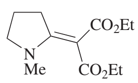
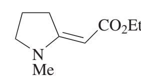
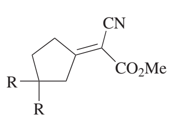
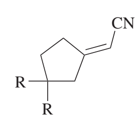
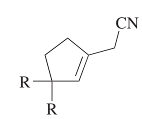
R	n	Solvent	Additive(s)	Temp (º)	Time (h)	
$(4\text{-}MeC_6H_4)O_2S$	1	DMF	LiI, NaCN	120	20	(58)
$(4\text{-}MeC_6H_4)O_2S$	1	HMPA	$Me_4N^+AcO^-$	100	7	(47)
$(4\text{-}MeC_6H_4)O_2S$	1	DMF	Cs_2CO_3, 4-$H_2NC_6H_4SH$	85	1	(97)
$(4\text{-}MeC_6H_4)O_2S$	2	DMF	Cs_2CO_3, 4-$H_2NC_6H_4SH$	85	5	(92)
2-Me-3,4,5,6-$(MeO)_4C_6$	1	DMF	H_2O, NaCl	153	15	(26)
2-Me-3,4,5,6-$(MeO)_4C_6$	1	DMF	LiI, NaCN	120	15	(28)
2-Me-3,4,5,6-$(MeO)_4C_6$	1	DMF	CsOAc	130	24	(47)
2-Me-3,4,5,6-$(MeO)_4C_6$	1	HMPA	$Me_4N^+AcO^-$	100	24	(62)
2-Me-3,4,5,6-$(MeO)_4C_6$	1	DMF	Cs_2CO_3, PhSH	85	1	(73)
2-Me-3,4,5,6-$(MeO)_4C_6$	1	DMF	Cs_2CO_3, 4-$H_2NC_6H_4SH$	85	1	(98)

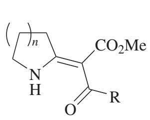
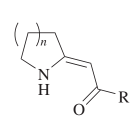
TABLE 17. DEALKOXYCARBONYLATIONS OF α-SULFONYL AND α-SULFOXIMINO ESTERS (*Continued*)

α-Sulfonyl or α-Sulfoximino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21} 	DMF, PhSH, Cs_2CO_3, 90°, 4.25 h	 (87)	1876
$C_{27–54}$ 	DMF, PhSH, Cs_2CO_3, 85°, 3 h	*m* *n*	
		0 0 (91)	1877, 1878
		1 0 (87)	1877
		0 1 (89)	1877
		1 1 (85)	1877
		1 2 (82)	1877
			
C_{28} 	HMPA, $Me_4N^+AcO^-$, 100–105°, 15 h	 (78)	719
C_{60} 	DMF, PhSH, Cs_2CO_3, 85°, 1 h	 (83)	1875, 547

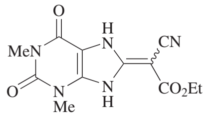
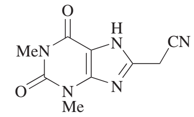
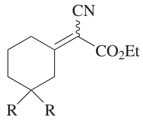
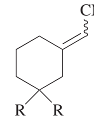
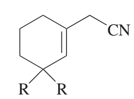
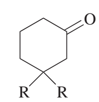
[a] The configuration was assigned on the assumption that protonation of the intermediate enolate occurs from the less hindered side.

TABLE 18. DEALKOXYCARBONYLATIONS OF ALKYLIDENE DERIVATIVES OF ACTIVATED ESTERS

Alkylidene Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	Sulfolane, KCl, dicyclohexyl-18-crown-6, 150°, 30 min	 (70)	733
C_5 	Sulfolane, KCl, dicyclohexyl-18-crown-6, 150°, 30 min	 R: NC (16); MeO_2C (7)	733
$C_{6–7}$ 	DMSO, H_2O, NaCl, 180°, 30 min	 R: H (48); Me (—)	215
C_7 	$EtCO_2H$, reflux, 48 h	 (0)	322
	n-$C_7H_{15}CO_2H$, (n-Bu)$_4$PBr, 200°, 4 h	 (82)	321
	Al_2O_3 (acidic), 120°, 1 h	 (31)	1879
$C_{8–10}$ 	DMSO, H_2O, NaCl, 160°, 6 h	 +  R: H, I + II (55–66), I/II 3:1; Me, I + II (55–66), I/II 4:1	214

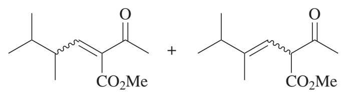
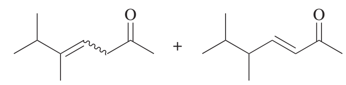
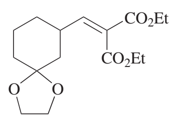
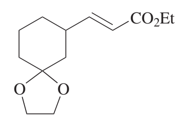
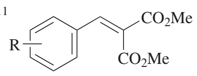
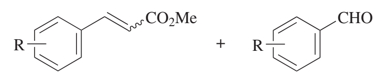
Alkylidene Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{8–15}$ 	$B(OH)_3$, 225°, 1 h		1880

n	R	
1	Me	(50)
1	n-Pr	(46)
1	Ph	(60)
2	Me	(43)
2	n-Pr	(30)
2	Ph	(50)
3	Me	(39)
3	n-Pr	(40)
3	Ph	(27)

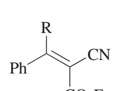
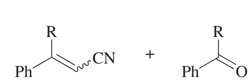
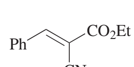
Alkylidene Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	DMF, reflux, 2 h	 (90)	1881
$C_{9–11}$ 	DMSO, H_2O, additive	 I +  III +  III	

R	Additive	Temp (°)	Time (h)	I	II	I/II	III	Refs.
H	NaCl	160	6	(55–66)		1:2	(20)	214
Me	LiCl	160–165	—	(72)	(—)	—	(—)	1882

TABLE 18. DEALKOXYCARBONYLATIONS OF ALKYLIDENE DERIVATIVES OF ACTIVATED ESTERS (*Continued*)

Alkylidene Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}  **I** (*E*)/(*Z*) = 1.5:1 **II** (*E*)/(*Z*) = 1.5:1 **I/II** = 3:1	DMSO, H_2O, LiCl, 135–142°, 2 h	 **III** (*E*)/(*Z*) = 2.2:1 **IV** **III** + **IV** (77), **III/IV** = 13:1	1883
	DMSO, H_2O, NaCl, 150–170°, 5 h	 "low yield"	1884
C_{10-11} 	See table.	 **I** + **II**	

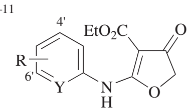
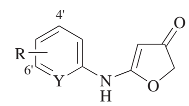
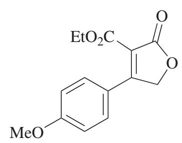
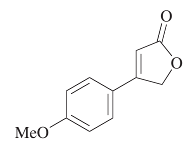
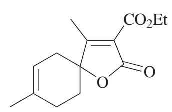
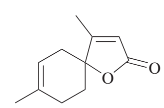
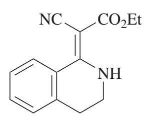
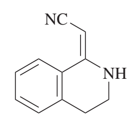
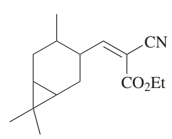
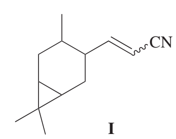
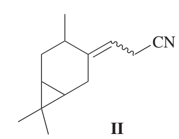
R	Solvent	Additive(s)	Temp (°)	Time (h)	**I**[a]	*E/Z*	**II**[a]	Refs.
H	DMF	NaCl	reflux	23	(75)	92:8	(3)	212
H	DMF	NaBr	reflux	23	(90)	69:31	(0)	212
H	DMSO	—	165	6	(3)	75:25	(11)	212, 1885
H	DMSO	H_2O, NaCl	165	6	(53)	99:1	(15)	212, 1885
H	DMSO	H_2O, NaCl	reflux	6	(76)	99:1	(—)	212
H	DMSO	H_2O, NaBr	165	6	(55)	82:16	(13)	212, 1885
H	n-$C_7H_{15}CO_2H$	(n-Bu)$_4$PBr	200	16	(91)	—	(—)	321
4-O_2N	DMSO	H_2O, NaCl	165	6	(42)	98:2	(10)	212
4-O_2N	DMSO	H_2O, NaBr	165	6	(40)	85:15	(12)	212
2-MeO	DMF	NaCl	reflux	23	(30)	70:30	(3)	212
2-MeO	DMF	NaBr	reflux	23	(38)	60:40	(0)	212
2-MeO	DMSO	H_2O, NaCl	165	6	(50)	80:20	(15)	212
2-MeO	DMSO	H_2O, NaBr	165	6	(61)	78:22	(17)	212
4-MeO	DMF	NaCl	reflux	23	(72)	91:9	(4)	212
4-MeO	DMF	NaBr	reflux	23	(90)	78:22	(0)	212
4-MeO	DMSO	H_2O, NaCl	165	6	(58)	96:4	(20)	212
4-MeO	DMSO	H_2O, NaBr	165	6	(60)	90:10	(16)	212
2-i-PrO	DMSO	H_2O, NaCl	165	6	(53)	76:24	(19)	212
2-i-PrO	DMSO	H_2O, NaBr	165	6	(30)	75:25	(11)	212
2-Me	DMF	NaCl	reflux	23	(45)	75:25	(6)	212
2-Me	DMF	NaBr	reflux	23	(50)	72:28	(0)	212
2-Me	DMSO	H_2O, NaCl	165	6	(53)	71:29	(14)	212
2-Me	DMSO	H_2O, NaBr	165	6	(30)	85:15	(13)	212
4-Me	DMSO	H_2O, NaCl	165	6	(54)	98:2	(16)	212
4-Me	DMSO	H_2O, NaBr	165	6	(52)	85:15	(15)	212

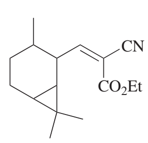
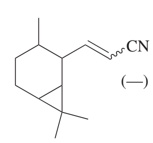
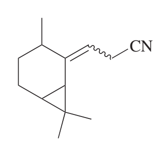
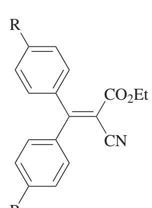
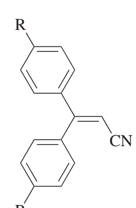
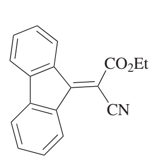
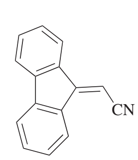
Alkylidene Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, 160°, 6 h	 **I** + **II**	214
C_{10} 	DMSO, additive(s), 165°, 3 h	 **I** + **II**	213

R	**I**	**II**
H	(55–66)	(20)
Me	(55–66)	(20)

Additive(s)	**I** + **II**	**I/II**
H_2O, LiCl	(63)	3:2
NaCl	(51)	3:1

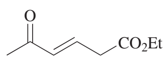
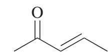
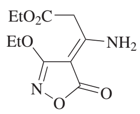
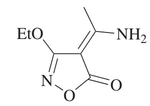
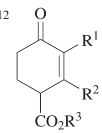
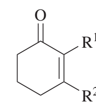
TABLE 18. DEALKOXYCARBONYLATIONS OF ALKYLIDENE DERIVATIVES OF ACTIVATED ESTERS (*Continued*)

Alkylidene Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11}			
	DMF, reflux, 6 h	 Y / R: N, H (55); N, 4'-Me (57); N, 6'-Me (55); CH, H (55)	1886
C_{11}			
	DMSO, H_2O, NaCl, 120–130°, 6 h	 (91)	1887
C_{12}			
	DMSO, H_2O, NaCl, 160°, 2 h	 (90)	1056
	DMSO, H_2O, LiCl, reflux, 5–6 h	 (60)	1888
C_{14}			
	DMSO, H_2O, NaCl, reflux, 4 h	 **I** +  **II** **I** + **II** (42), **I/II** = —	1889

Alkylidene Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMSO, H_2O, NaCl, reflux, 4 h	 (—) +  (—)	1889
C_{16}			
	DMSO, H_2O, NaCl, 160–170°, 4 h	 R: H (72); F (70–75); Cl (70–75)	1890
	DMSO, H_2O, NaCl, 160–170°, 4 h	 (72)	1890

[a] The yields were determined by gas chromatography.

TABLE 19. VINYLOGOUS AND PHENYLOGOUS DEALKOXYCARBONYLATIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	o-Xylene, DABCO, reflux, 6 h	 (96)	298
	DMSO, H_2O, NaCl, 150°	 (36)	1891
C_{8-12} 	See table.		

R^1	R^2	R^3	Solvent	Additive	Temp	Time (h)		
H	Me	Me	H_2O	Dowex 50	reflux	12	(83)	1595
H	Me	Et	dioxane	H_2O, Al_2O_3	reflux	140	(72)	310
H	Me	Et	o-xylene	DABCO	reflux	6	(96)	298
H	Me	Et	o-xylene	3-quinuclidinol	reflux	4	(98)	294
H	Me	Et	o-xylene	brucine	reflux	24	(28)	883
H	Me	Et	o-xylene	tropine	reflux	24	(25)	883
H	Me	Et	o-xylene	nicotine	reflux	24	(25)	883
H	Me	Et	o-xylene	reserpine	reflux	24	(35)	883
H	Me	Et	o-xylene	yohimbine•HCl	reflux	24	(14)	883
H	Me	Et	o-xylene	quinidine	reflux	24	(57)	883
Et	Me	Et	o-xylene	DABCO	reflux	6	(96)	298
Et	Me	Et	o-xylene	3-quinuclidinol	reflux	4	(96)	294
Et	Me	Et	o-xylene	quinine•H_2O	reflux	20	(90)	882
Et	Me	Et	o-xylene	perloline•HCl	reflux	48	(0)	882
EtO_2CCH_2	Me	Et	DMSO	H_2O, NaCl	180–190°	5	(70)	216
$Me_2C{=}CHCH_2$	H	Et	DMSO	H_2O, NaCl	190°	10	(78)	1892

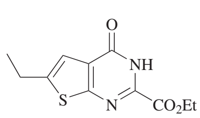
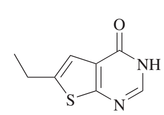
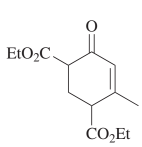
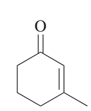
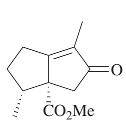
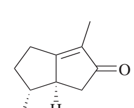
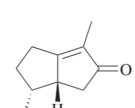
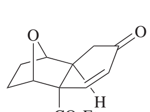
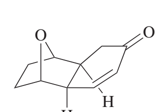
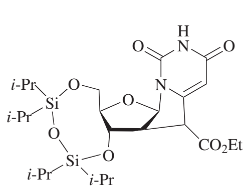
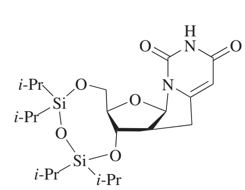
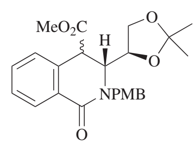
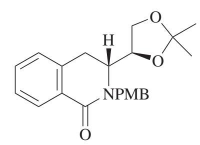
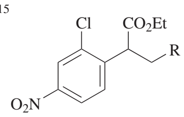
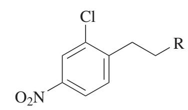
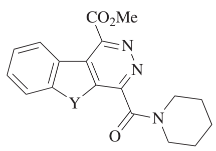
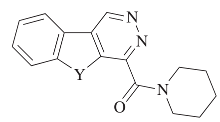
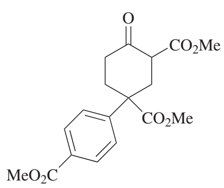
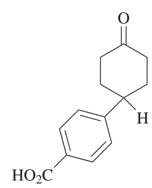
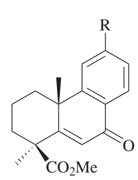
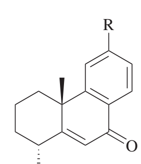
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	DMSO, LiCl, 150°	 (—)	1893
	H_2O, 160°	 (—)	1569
C_{11} 	DMF, LiI•$3H_2O$, reflux, 1 d	 I +  II; **I** + **II** (90), **I**/**II** = 5:4	269, 270, 268
	DMSO, H_2O, NaCl, 180°, 9 h	 (20)[a]	524
	DMSO, H_2O, NaCl, 145°, 6 h	 (32)	1894

TABLE 19. VINYLOGOUS AND PHENYLOGOUS DEALKOXYCARBONYLATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}  α or β CO_2Me	Krapcho	 (—)	1895
C_{12-15} 	DMSO, H_2O, NaCl, 155°, overnight	 R: $AcCH_2$ (56); Ph (85)	146
C_{12} 	DMF, LiI, reflux	 Y: HN (45); O (59)	218
C_{15} 	DMSO, NaCN, 180–185°, 2 h	 (73)	1653
C_{17} 	See table.		

R	Solvent	Additive	Temp	Time (h)		Refs.
H	2,4,6-collidine	LiI	reflux	10	(100)	1896
HO	2,4,6-collidine	LiI	reflux	10	(31)	1896
MeO	*o*-xylene	3-quinuclidinol	reflux	6	(93)	294
MeO	*o*-xylene	DBN	reflux	6	(78)	292
MeO	*o*-xylene	DBU	165°	5	(92)[b]	293
MeO	*o*-xylene	DABCO	reflux	6	(90)	298

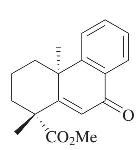
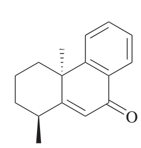
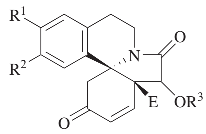
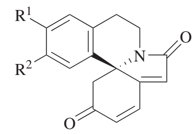
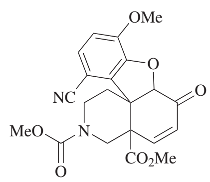
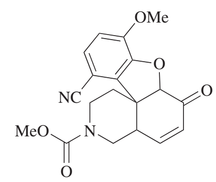
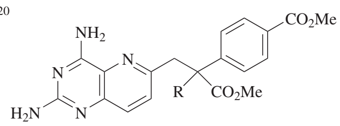
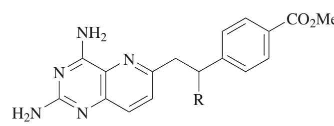
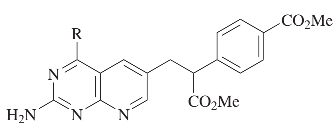
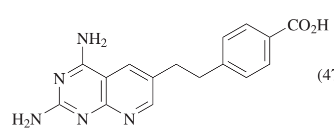
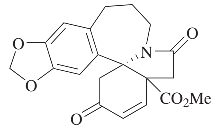
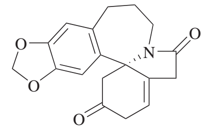
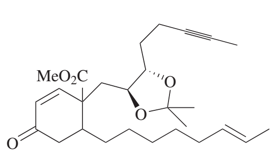
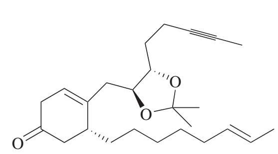
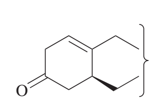
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	2,4,6-Collidine, reflux, 10 h	 (—)	1896

TABLE 19. VINYLOGOUS AND PHENYLOGOUS DEALKOXYCARBONYLATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}  E = CO_2Me	DMSO, additive(s)		

R^1	R^2	R^3	Additive(s)	Temp (°)	Time (h)		Refs.
H	H	Ms	$MgCl_2$	160	2	(68)	266
H	MeO	Ms	$MgCl_2$	160	2	(89)	266
MeO	MeO	H	H_2O, NaCl	140	10	(19)	1897
MeO	MeO	H	$MgCl_2$	130	2	(40)	1897
MeO	MeO	Ac	$MgCl_2$	144	2	(17)	1897
MeO	MeO	Ms	$MgCl_2$	140	2.5	(89)	1897
–OCH_2O–		Ms	$MgCl_2$	144	2	(82)	1897

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Dioxane, H_2O, Al_2O_3, reflux[c]	 (26)	319
C_{17-20} 	DMSO, H_2O, NaCN, 175–180°, 2.5 h	 R: H (—); Me (96); Et (—); *n*-Pr (—)	1898

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}  mixture of R = NH_2 and R = N=$CHNMe_2$	DMSO, NaCN, 180–190°, 2.5 h	 (47)	1899
C_{18} 	DMSO, *t*-$C_7H_{15}SH$, $CaCl_2$, 160°, 1 h	 (83)	217
C_{23} 	1. *t*-BuOK, THF, H_2O, rt, 5 h 2. 105°, 5–10 min	 **I** (51) +  **II** (16)	1900
	DMSO, NaCl	**I** + **II** (—)[d]	1900
	HMPA, NaH, PhSeH	**I** + **II** (—)[d]	1900

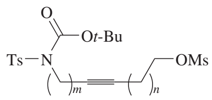
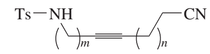
[a] An additional 20% of starting material was recovered.

[b] The substrate was the 2-bromo saturated ketone.

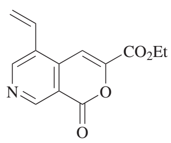
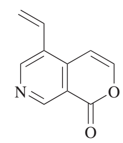
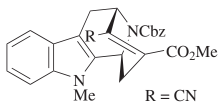
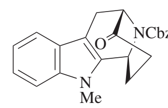
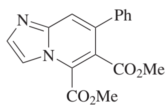
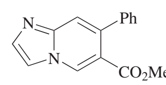
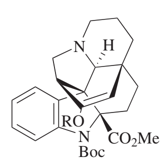
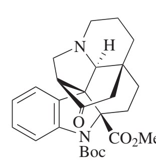
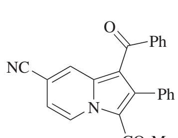
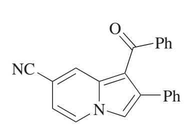
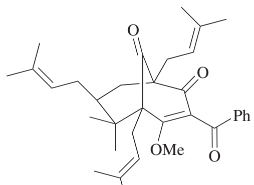
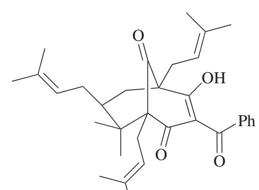
[c] The following conditions led to decomposition: *o*-xylene with DBN, DBU, DABCO, or quinuclidine; DMSO, H_2O, NaCl; collidine, LiI.

[d] Tars were obtained.

TABLE 20. MISCELLANEOUS DEALKOXYCARBONYLATIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-9}			
	NaCN		219

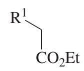
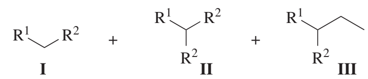
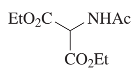
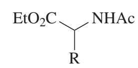
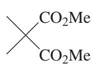
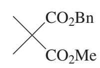
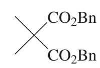
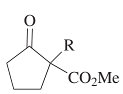
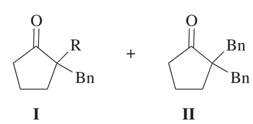
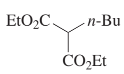
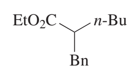
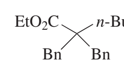
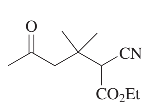
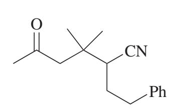
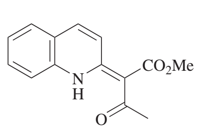
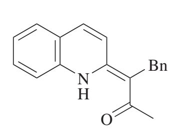
m	*n*	Solvent	Temp (°)	Time	
2	2	DMSO	90	overnight	(45)
3	2	DMF	80	24 h	(81)[a]
3	3	DMF	80	24 h	(69)[a]

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMF, H_2O, NaCl, reflux, 3 d	 (12)	1901
C_{15}			
 R = CN	DMF, H_2O, NaCl, 130°, 8 h	 (68)	1668, 1669
	DMSO, H_2O, NaCl, 150°, 5 h	 (61)	1902
C_{20}			
 R = Boc	DMSO, H_2O, LiCl, 100–110°, 6 h	 (61)	220
C_{23}			
	DMSO, H_2O, NaCl, 150°, 20 h	 (90)	1903
C_{33}			
	DMSO, H_2O, LiCl, 120°, 2 h	 (57)	1904

[a] The yield includes that of the two-step preparation of the substrate.

TABLE 21. DEALKOXYCARBONYLATIVE TRAPPING IN THE PRESENCE OF OTHER ELECTROPHILES

A. ALKYLATIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-4} 	R^2Br (*x* eq), HMPA, LiCl		21
C_3 	RBr, HMPA, LiCl, 150–160°, 1–1.5 h		21
C_5 	BnBr, HMPA, LiCl, 155°, 1 h	 (30)[a] +  (18)[a]	21
C_{6-7} 	BnBr, HMPA, LiCl, 160°		21
C_7 	BnBr, HMPA, LiCl, 155°, 1.5 h	 (71)[a] +  (10)[a]	21
C_9 	1. HMPA, LiCl, 150°, 1 h 2. $PhCH_2CH_2Br$, 160°, 6 h	 (20)	1839
C_{13} 	BnBr, HMPA, LiBr, 135°, 2 h	 (39)	221

C$_{3-4}$ entry:

R^1	R^2	*x*	Temp (°)	Time (h)	I[a]	II[a]	III[a]
NC	Bn	0.83	140	2	(15)	(52)	(0)
NC	Bn	0.83	160	1	(30)	(64)	(0)
NC	n-C_8H_{17}	0.83	160	1	(16)	(4)	(0)
EtO_2C	Bn	0.5	160	1	(60)	(14)	(13)
Ac	Bn	0.83	160	1.5	(24)	(0)	(0)

C$_3$ entry:

R	[a]
Bn	(52)
n-C_8H_{17}	(22)

C$_{6-7}$ entry:

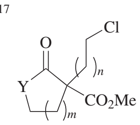
R	Time (min)	I[a]	II[a]
H	20	(47)	(10)
Me	15	(35)	(0)

[a] Yields are based on the alkyl halide.

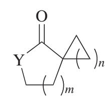
B. CYCLIZATIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{8-17}



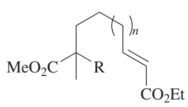
HMPA[a], LiCl, 125–140°



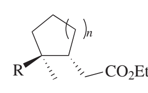
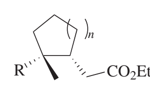
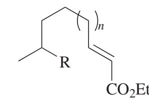
Y	*m*	*n*	Time (h)	
CH_2	1	1	1	(64)
CH_2	1	3	1	(75)
CH_2	2	3	1	(68)
CH_2	3	3	1.5	(70)
CH_2	8	3	1.5	(71)
O	1	3	1–1.5	(69)

Refs. 223

C_{9-11}



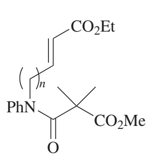
HMPA, LiCl, 120°, 4 h


I
+

II
+

III

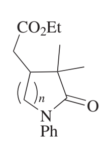
n	R	I + II + III	I/II/III
1	PhO_2S	(91)	99:1:0
1	NC	(67)	77:23:0
1	MeCO	(94)	93:7:0
1	EtO_2C	(64)	74:26:0
1	PhCO	(78)	89:11:0
2	PhO_2S	(82)	80:5:15
2	NC	(45)	69:15:16
2	MeCO	(55)	64:12:24
2	EtO_2C	(—)[b]	40:10:26
2	PhCO	(76)	74:2:24

Refs. 225

C_{9-10}



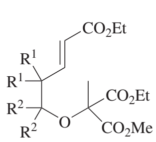
DMEU, LiI, 100°, 4–8 h



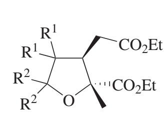
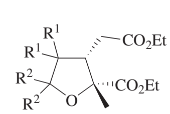
n	
1	(34)
2	(82)

Refs. 111

C_{9-11}



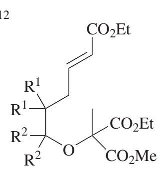
DMEU, LiI, 120°, 4–8 h


I
+

II

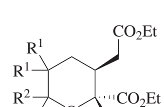
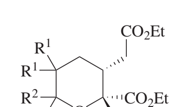
R^1	R^2	I + II	I/II
H	H	(67)	76:24
H	Me	(67)	60:40
Me	H	(60)	84:16

Refs. 1905

C_{10-12}



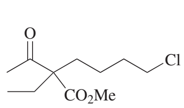
DMEU, LiI, 120°, 4–8 h


I
+

II

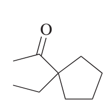
R^1	R^2	I + II	I/II
H	H	(93)	88:12
H	Me	(75)	81:19
Me	H	(72)	81:19

Refs. 1905

C_{10}



HMPA, LiCl, 125–140°, 1–1.5 h


(80)

Refs. 223

TABLE 21. DEALKOXYCARBONYLATIVE TRAPPING IN THE PRESENCE OF OTHER ELECTROPHILES (*Continued*)

B. CYCLIZATIONS (*Continued*)

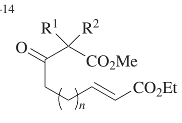
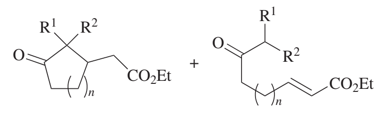
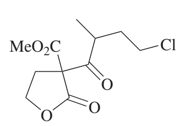
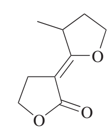
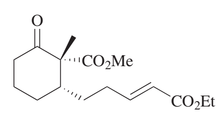
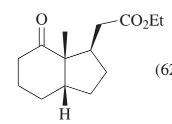
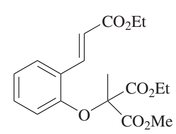
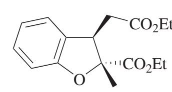
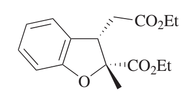
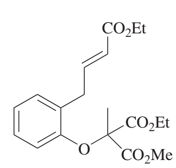
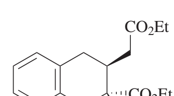
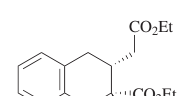
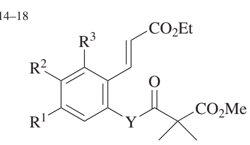
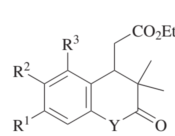
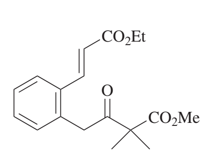
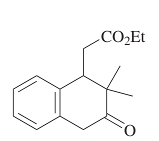
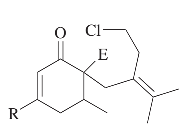
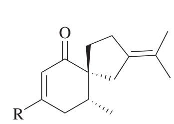
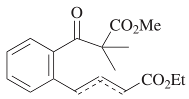
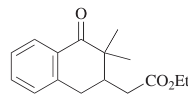
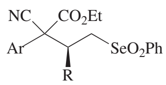
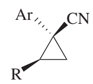
<table>
<tr><th>Substrate</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_{10-14}
</td><td>HMPA, LiCl, 120°, 4 h</td><td>
<table><tr><th>n</th><th>R^1</th><th>R^2</th><th>I</th><th>II</th></tr><tr><td>1</td><td>Me</td><td>Me</td><td>(24)</td><td>(52)</td></tr><tr><td>2</td><td>Me</td><td>Me</td><td>(74)</td><td>(0)</td></tr><tr><td>2</td><td colspan="2">$-(CH_2)_4-$</td><td>(63)</td><td>(0)</td></tr><tr><td>2</td><td colspan="2">$-(CH_2)_5-$</td><td>(60)</td><td>(0)</td></tr></table></td><td>1906</td></tr>
<tr><td>C_{10}
</td><td>HMPA, LiCl, 120°, 5 min;
then 130°, 10 min</td><td> (61)</td><td>222</td></tr>
<tr><td>C_{13}
</td><td>DMPU, LiCl, 120°, 6 h</td><td> (62) >20:1 dr</td><td>1907</td></tr>
<tr><td></td><td>DMEU, LiI, 120°, 4–8 h</td><td>
I
+

II
I + **II** (84), **I/II** = 84:16</td><td>1905</td></tr>
<tr><td>C_{14}
</td><td>DMEU, LiI, 120°, 4–8 h</td><td>
I
+

II
I + **II** (76), **I/II** = 80:20</td><td>1905</td></tr>
<tr><td>C_{14-18}
</td><td>DMEU, LiCl,
100°, 4–8 h</td><td>
<table><tr><th>Y</th><th>R^1</th><th>R^2</th><th>R^3</th><th></th></tr><tr><td>HN</td><td>H</td><td>H</td><td>H</td><td>(76)</td></tr><tr><td>O</td><td>H</td><td>H</td><td>H</td><td>(62)</td></tr><tr><td>O</td><td>MeO</td><td>H</td><td>H</td><td>(50)</td></tr><tr><td>O</td><td>Me</td><td>H</td><td>H</td><td>(48)</td></tr><tr><td>O</td><td>H</td><td colspan="2">$-(CH{=}CH)_2-$</td><td>(52)</td></tr></table></td><td>111</td></tr>
<tr><td>C_{15}
</td><td>HMPA, LiCl, 120°, 4 h</td><td> (63)</td><td>1906</td></tr>
<tr><td>
E = CO_2Me</td><td>HMPA, LiCl,
125–140°, 4–8 h</td><td>
<table><tr><th>R</th><th></th><th>dr</th></tr><tr><td>H</td><td>(80)</td><td>9:1</td></tr><tr><td>*i*-PrO</td><td>(98)</td><td>9:1</td></tr></table></td><td>223</td></tr>
</table>

TABLE 21. DEALKOXYCARBONYLATIVE TRAPPING IN THE PRESENCE OF OTHER ELECTROPHILES (*Continued*)

B. CYCLIZATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)					Refs.
C_{15}							
	HMPA, LiCl, 120°, 4 h	 (46)					1906
C_{17-18}							
	HMPA, LiCl, 80°, 2–4 h		Ar	R	[c]	er	224
			Ph	Ph	(65)	83.0:17.0	
			Ph	3-FC_6H_4	(55)	87.0:13.0	
			Ph	4-ClC_6H_4	(40)	86.0:14.0	
			Ph	4-$MeOC_6H_4$	(64)	83.0:17.0	
			Ph	*n*-C_6H_{13}	(90)	77.0:23.0	
			Ph	*n*-C_6H_{13}	(81)[d]	74.0:26.0	
			4-$MeOC_6H_4$	*n*-C_6H_{13}	(91)	76.0:24.0	
			4-FC_6H_4	4-ClC_6H_4	(42)	87.0:13.0	
			5-BrC_6H_4	Ph	(52)	80.5:19.5	
			Ph	2-MeC_6H_4	(56)	74.0:26.0	
			Ph	4-MeC_6H_4	(51)	84.0:16.0	

[a] Use of 2-pyrrolidone as the solvent gave similar results but DMF was less satisfactory.

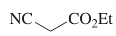
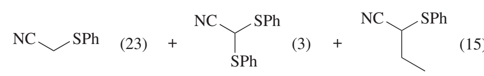
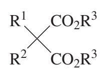
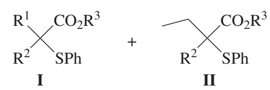
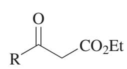
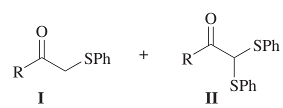
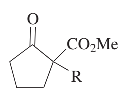
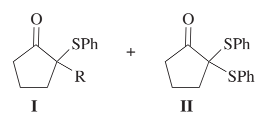
[b] The product was a complex mixture.

[c] The yield is for the one-pot reaction of the preparation of the substrate and the cyclization.

[d] The reaction was carried out at –20° for 6d.

TABLE 21. DEALKOXYCARBONYLATIVE TRAPPING IN THE PRESENCE OF OTHER ELECTROPHILES (*Continued*)

C. MISCELLANEOUS REACTIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	PhSSPh, HMPA, NaI, 160–170°, 1 h	 (23) + (3) + (15)	226
C_{3-17} 	PhSSPh, HMPA, NaI, 160–170°, 1 h		226
C_{4-9} 	PhSSPh, HMPA, NaI, 160–170°, 1 h		226
C_{6-7} 	PhSSPh, HMPA, NaI, 160–170°, 1 h		226

C_{3-17} products:

R^1	R^2	R^3	**I**	**II**
H	H	Et	(84)	(8)
Me	Me	Me	(71)	(0)
Me	*n*-Pr	Et	(60)	(0)
n-Bu	H	Et	(40)	(0)
Bn	H	Et	(46)	(0)
Bn	Bn	Et	(66)	(0)

C_{4-9} products:

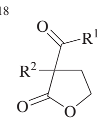
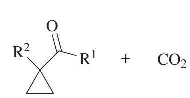
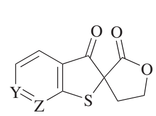
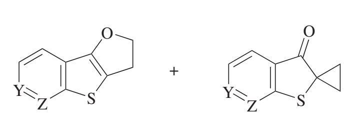
R	**I**	**II**
Me	(67)	(8)
Ph	(36)	(0)

C_{6-7} products:

R	**I**	**II**
H	(47)	(5)
Me	(49)	(0)

TABLE 21. DEALKOXYCARBONYLATIVE TRAPPING IN THE PRESENCE OF OTHER ELECTROPHILES (*Continued*)

C. MISCELLANEOUS REACTIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-18} 	See table.	 + CO_2	227
C_{10} 	DMSO, NaCl	 major	1908

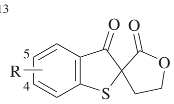
C_{6-18} conditions and yields:

R^1	R^2	Solvent	Additive	Temp (°)	Time (h)	
Me	H	DMF	NaBr	reflux	59	(52)
Ph	H	DMSO	—	160	6	(0)[a]
Ph	H	DMSO	NaCl	160	6	(69)
Ph	H	DMSO	NaBr	160	6	(92)
Ph	H	DMF	NaBr	reflux	6	(73)
Ph	H	DMSO	NaI	160	6	(77)
Ph	H	DMSO	KCl	160	6	(50)
Ph	H	DMSO	Me_4NBr	160	6	(58)
Ph	H	*o*-xylene	DABCO	reflux	6	(62)
Ph	Me	DMSO	NaCl	160	12	(82)
Ph	Bn	DMSO	NaCl	160	10	(100)
c-C_6H_{11}	H	DMF	NaBr	reflux	55	(70)
4-ClC_6H_4	H	DMSO	NaCl	160	8	(69)
4-$MeOC_6H_4$	H	DMSO	NaCl	160	9	(61)
4-MeC_6H_4	H	DMSO	NaCl	160	9	(74)
Bn	H	DMSO	NaBr	160	8	(65)

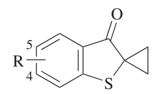
C_{10} products:

Y	Z	
CH	N	(—)
N	CH	(—)

C_{11-13}

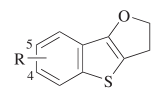


DMSO, NaCl, 155–160°, 3.5 h

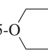


I

+



II

R	I	II	R	I	II
H	(79)	(4)	5-Cl	(—)	(—)[b]
5-H_2N	(—)[b]	(—)	5-O_2N	(—)	(—)[b]
5-MeS	(—)[b]	(—)	5-MeO_2S	(—)	(—)[b]
4,5-$(MeO)_2$	(—)[b]	(—)	5-ONO_2S	(—)	(—)[b]
5-Me	(—)[b]	(—)	5-MeCO	(—)	(—)[b]

1908

[a] The starting material was recovered.

[b] This was the predominant product.

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