CHAPTER 1

CATALYTIC, ASYMMETRIC, INTRAMOLECULAR CARBON–HYDROGEN INSERTION

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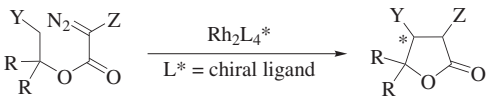
INTRODUCTION

Among the most synthetically attractive methods for replacement of hydrogen on carbon are those that form new C–C bonds and, among these methods, controlled insertion of a metallo-carbene into a C–H bond has broad applications. This strategy has become popular, in large part, due to advances in

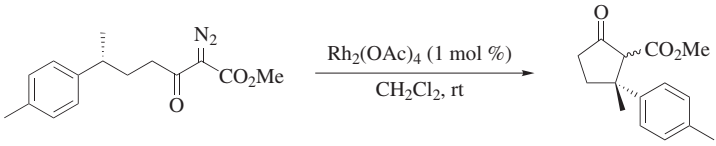
our understanding of metallo-carbene chemistry and the evolution of its catalytic applications[1–21] over the past sixty years from an impractical curiosity to a useful strategy in synthetic organic chemistry.[7,12–14,18,19,22–32] Intramolecular reactions of metallo-carbenes with remote C–H bonds were the first to be investigated as synthetic strategies; they provide access to more complex materials by selective functionalization at a normally unreactive C–H site (e.g. Eq. 1).[2–7,12–19,31] Site- and stereoselective discrimination among the C–H bonds found in complex molecules is critical to the ultimate success of these strategies. Advances in the development and applications of catalyst systems that selectively insert a carbene into a specific C–H bond have been the subject of intensive investigations,[6,7,13,18,19,24,25,31,32] and the intramolecular applications of this method are the subject of this chapter.



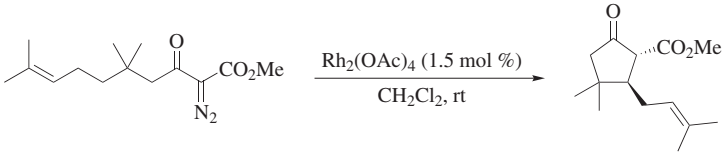
(Eq. 1)

Although C–H insertion reactions of free carbenes have been known for several decades, it has only been through the application of metallo-carbenes that highly selective, high-yielding C–H insertions could be realized.[33–38] Copper catalysts were employed prior to the initial reports of insertion reactions with dirhodium(II) carboxylate catalysts, but they showed limited success except with highly constrained systems.[39] These insertion reactions were carried out with α-diazocarbonyl compounds; the latter are ideally suited in view of their ready availability and their ability to undergo diazo decomposition to metallo-carbenes in reactions with selected transition-metal complexes.[32,40,41] Unlike their aliphatic diazoalkane counterparts, α-diazocarbonyl compounds are conveniently prepared and relatively stable to thermal and acid-promoted decomposition. The intermediate metallo-carbenes generated from diazocarbonyl compounds by reactions with transition-metal complexes are able to react in a selective fashion with C–H bonds.[26,42,43]

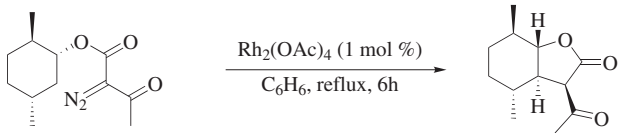
Although considerable attention has been devoted to reactions of α-diazocarbonyl compounds with transition-metal catalysts, including those of copper, silver, and gold,[14,18,44,45] ruthenium,[46–48] and even iron,[49–51] only dirhodium(II) catalysts have provided a consistent, dependable, and reproducible foundation for C–H insertion chemistry. Beginning in the 1990's with the development of dirhodium(II) catalysts having chiral carboxylate[52–54] and carboxamidate ligands,[32,55] stereocontrol has been a primary focus of this research. Chiral catalysts are capable of providing high levels of enantioselectivity, as well as diastereo- and site-selectivity, and they are the focus of this chapter. Although C–H insertion reactions using achiral catalysts are common in organic synthesis (Eq. 2–4) and exhibit high site- and diastereoselectivity,[32,56] this review will be devoted to C–H insertion reactions that utilize chiral catalysts to exert stereocontrol over the insertion process.



(67%) (Eq. 2)



(77%) (Eq. 3)



(87%) (Eq. 4)

The first reports of asymmetric C–H insertion reactions focused on intramolecular processes.[32,40,42,56] Intermolecular C–H insertion reactions were subsequently found to be controllable and synthetically useful,[57,58] and a recent related chapter[59] provides a comprehensive overview of enantioselective intermolecular C–H insertion reactions.

In contrast to cyclopropanation reactions, for which a variety of transition-metal complexes are effective catalysts,[32,42,60–62] dirhodium(II) compounds have emerged as the dominant catalyst class for C–H insertion reactions. The dirhodium(II) catalysts are paddlewheel-shaped dimetallic complexes in which four bidentate ligands bridge two rhodium atoms connected by a rhodium–rhodium bond and completed by two axial ligands (Fig. 1). The bridging ligands are most commonly carboxylates or carboxamidates, although asymmetric catalysts based on phosphonate[63,64] and arylphosphine[65–68] ligands have also been reported. With identical substitution on each rhodium atom, the two axial faces of the paddlewheel-shaped complex of the dirhodium(II) catalysts are homotopic, provided the complex has D_2 symmetry. A large number of enantiomerically enriched dirhodium complexes have been reported, but only a few have found widespread application for asymmetric C–H insertion.[25,53,69,70] Due to their stability to ambient air and moisture, these complexes are convenient to store and use.

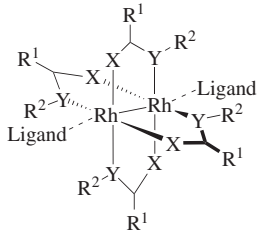


Figure 1. Dirhodium (II) paddlewheel complexes.

Because α-diazocarbonyl compounds are the most common precursors to metal carbene intermediates in catalytic reactions, numerous methods for their preparation have been reported and reviewed.[32,40,71–82] Although caution should be exercised in the preparation and use of any diazo compound, α-diazocarbonyl compounds exhibit much greater thermal stability than the more reactive diazoalkanes.[32,71] Ethyl diazoacetate, for example, is stable for long periods at temperatures at or below 120° and does not undergo loss of dinitrogen in glacial acetic acid. Methyl phenyldiazoacetate is even more stable.[32] As evidenced by the extensive applications of α-diazocarbonyl compounds in synthesis,[32,40] simple precautions such as the use of well ventilated fume hoods and avoidance of high temperatures are sufficient to ensure the safe handling and use of α-diazocarbonyl compounds. Other compounds (e.g., iodonium ylides) have been explored for use as carbene precursors, in conjunction with transition-metal catalysts, in intramolecular C–H insertion reactions.[45,83–86]

Throughout this chapter we refer to the metal-catalyst-generated carbene species as a "metallo-carbene" rather than a "carbenoid". These intermediates have been observed, and they have been directly implicated in catalytic reactions.[87,88] Indeed, similarities exist between metal carbenes generated in copper and dirhodium(II) catalytic reactions and structurally well defined metallo-carbenes such as pentacarbonyltungstenphenyl carbene.[89,90] The term "carbenoid" was originally coined for α-haloalkyllithium compounds.[91] Although commonly used in reports of transition-metal-catalyzed reactions of diazo compounds, "carbenoid" implies more uncertainty in the structures of reaction intermediates than are revealed in mechanistic interpretations. The term "carbenoid" is used in this chapter only to infer uncertainty when appropriate to the discussion.

The "apparent C–H insertion" of metallo-carbenes into aryl C–H bonds is well known, but these reactions are unlikely to proceed through direct insertion into the aryl C–H bond.[32,92–94] Instead, the reaction is likely to be initiated by an electrophilic addition of the metal carbene onto the aromatic ring. Because these reactions are not the result of direct insertion into a C–H bond, they are not covered in this review.

Several reviews have focused on C–H insertion reactions of metal carbenes.[18,22,23,32,40,42,43,95,96] This review of catalytic, asymmetric, intramolecular C–H insertions, which covers the literature up to and including 2009, is organized according to the products obtained from the insertion reaction, focusing on functional groups.

MECHANISM AND STEREOCHEMISTRY

The catalytic cycle for conversion of a diazocarbonyl compound to a dirhodium-stabilized carbene, and subsequent transfer of the carbene, is believed to be applicable not only to dirhodium-stabilized carbene C–H insertion but to most, if not all, reactions of diazocarbonyl compounds using transition-metal catalysts.[32,41,56] Dirhodium(II) compounds are 18-electron rhodium complexes only when a ligand occupies the axial coordination site; axial ligands are Lewis

bases—commonly acetonitrile—that are ordinarily loosely held by dirhodium in solution [e.g., bis(acetonitrile)dirhodium(II) tetraacetate in Fig. 2].[97–104]

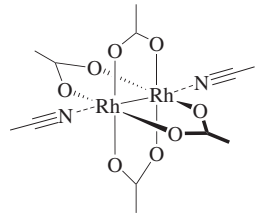
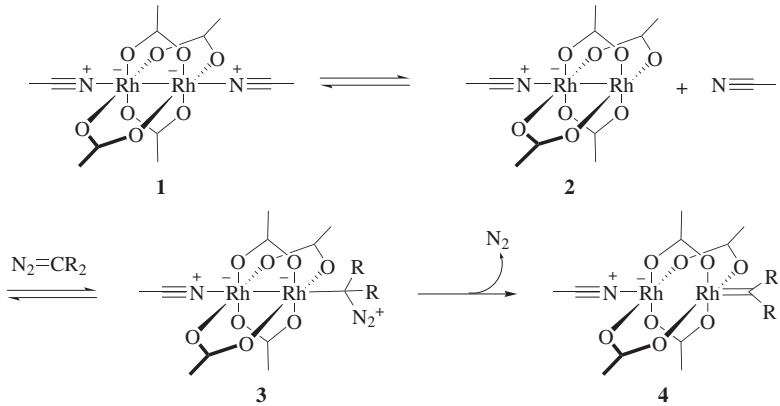


Figure 2. Dirhodium tetraacetate (bis)acetonitrile complex.

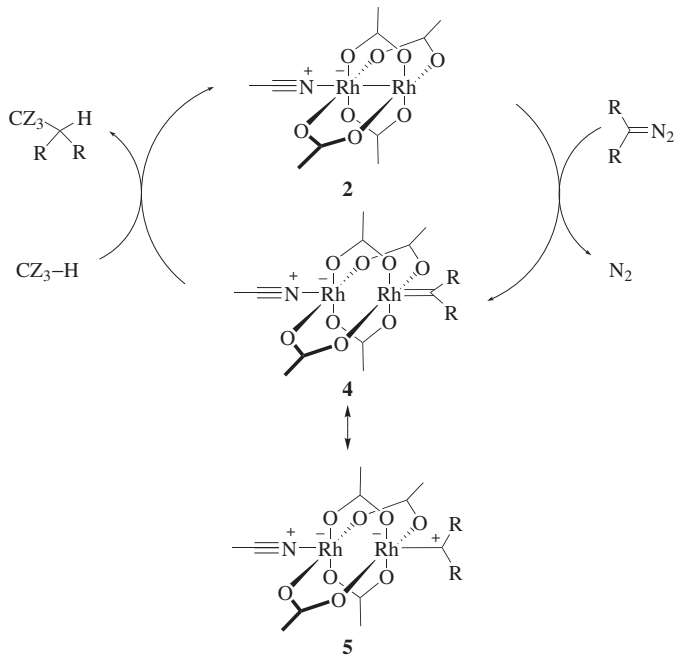
The metallo-carbene is produced by a sequence of steps beginning with ligand dissociation from dirhodium complex **1** and attack of the nucleophilic diazo carbon on the electron-deficient dirhodium(II) complex **2** (Scheme 1).[105–108]



Scheme 1

Back-bonding from rhodium to carbon aids the extrusion of dinitrogen from intermediate **3** and the formation of the dirhodium-stabilized carbene (**4**). Experimental and computational studies have identified the extrusion of dinitrogen as the rate-limiting step within the catalytic cycle.[106–109] Dinitrogen extrusion is first order in the dirhodium catalyst.[105,108] A large ^{15}N kinetic isotope effect for dinitrogen formation supports the mechanism outlined in Scheme 1.[110] The rhodium-stabilized carbene may be depicted by two resonance structures: one that describes a rhodium–carbon double bond (**4**, Scheme 2), not unlike that used to depict stable metal carbene complexes,[111–116] and another having a charge-separated structure (**5**) that places a formal positive charge on carbon and a formal negative charge on the metal.[32,117] The depiction of the carbene as a charge-separated species (metal-stabilized carbocation), while deemphasizing

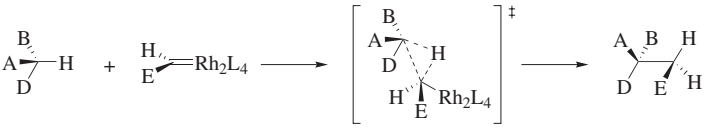
back-bonding from rhodium into the carbene, provides a simple tool with which to explain its electrophilic reactivity. Upon reaction of the metallo-carbene with a C–H bond, product formation occurs, and the catalyst is released back into the catalytic cycle. Kinetic isotope effects for C–H/C–D insertion are consistent with an increase in positive charge at the carbon of the C–H bond in the transition state,[58,118] and calculations have reproduced the experimental data.[107]



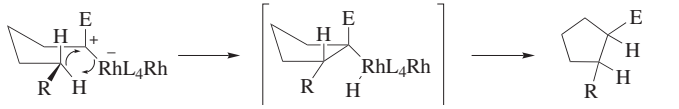
Scheme 2

The mechanism for insertion of a metal carbene into a C–H bond has generated considerable debate. Early studies provided evidence that insertion occurs with retention of configuration at carbon.[119,120] A primary point of contention had been whether insertion of the carbene into a C–H bond occurs through a three-centered transition state structure (concerted or stepwise)[58,107,121] or a four-centered transition state structure.[117,120,122–124] In the three-centered transition state structure (Eq. 5), the ligands at Rh do not dissociate, and the rhodium atom has no direct interactions with the C–H bond. The four-centered transition state (Eq. 6) implies a dissociation of a ligand from one rhodium site of the dirhodium intermediate; the reaction involves the addition of a C–H bond across the Rh–C bond to generate a metal-hydride species that undergoes reductive elimination.[117,120,124,125] Experimental[105,106,108] and computational[107,126] studies have evaluated these mechanistic proposals. No convincing evidence has been provided for a four-centered transition state, and kinetic data discount dissociation of a dirhodium ligand during the insertion process.[106] Recent computational

studies support these data and indicate that C–H insertion proceeds through a concerted, asynchronous, three-centered transition-state structure.[107] Accordingly, formation of the C–H bond occurs early in the transition state with subsequent C–C bond formation and release of the catalyst occurring concomitantly. The reaction is stereospecific at the C–H bond so that insertion occurs with retention of configuration.[32,107] Theoretical studies indicate that the second rhodium atom plays a critical role in the process, alternately accepting and donating electron density to the first rhodium atom during dinitrogen extrusion and C–C bond forming processes.[107] This bimetallic cooperativity is regarded as crucial to the success of C–H insertion and may explain the special role of dirhodium catalysts in carbene C–H insertion reactions.



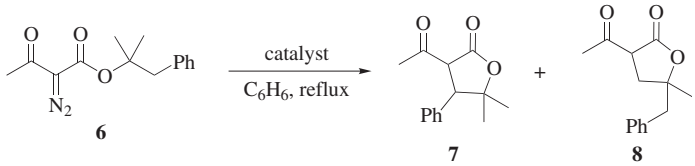
(Eq. 5)



(Eq. 6)

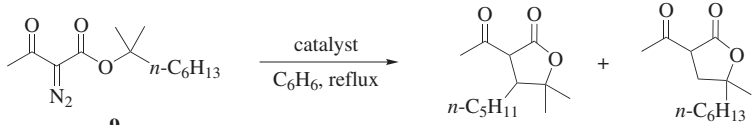
A buildup of positive charge occurs at the carbon from which hydrogen is transferred during insertion of the carbene into a C–H bond.[107] Consequently, substitution at the reacting C–H bond that stabilizes the developing positive charge lowers the activation energy, and promotes the insertion process.[105,120,121] This stabilization can lead to exceptional site selectivity for intramolecular C–H insertion. Early studies into the site selectivity of C–H insertion note a general trend of reactivity toward carbene insertion to be methine > methylene ≫ methyl C–H bonds.[120,121] Oxygen or nitrogen atoms also activate adjacent C–H bonds toward insertion.[127,128] Inverse selectivity from electron-withdrawing substituents has also been reported, with esters inhibiting insertion at C–H bonds that are α, and even β,[129] to the carbonyl carbon, although the latter has been disputed.[130] Surprisingly, an early competition study indicates that insertion into allylic and benzylic C–H bonds is disfavored;[120] however, more recent studies show that allylic and benzylic sites are preferentially reactive toward C–H insertion compared to their corresponding aliphatic counterparts.[58,131–133] Although the electronic effects of substituents are a powerful factor in determining the site selectivity of C–H insertion, steric and conformational effects also have substantial influence, especially when chiral dirhodium catalysts are employed.[121,134–136] An early example with 1,1-dimethyl-2-phenylethyl diazoacetoacetate (**6**) (Eq. 7) shows that insertion into the C–H bond of a methyl group (product **8**) occurs in preference to insertion into a benzylic C–H group (product **7**), independent of catalyst or temperature, whereas with 2-methyl-2-octyl diazoacetoacetate **9** (Eq. 8), site selectivity depends on the ligand (pfb = perfluorobutyrate; cap = caprolactamate) as indicated by the ratios of products **10** and **11**.[121] As is readily

apparent from subsequent examples that will be discussed, the choice of ligand can have an impact on site selectivity as well as stereoselectivity, and, not infrequently, chemoselectivity for C–H insertion vs. competing carbene-related processes.[121,137–142]



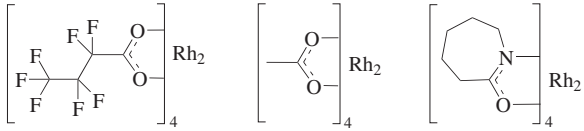
(Eq. 7)

Catalyst	Yield (%)	**7/8**
$Rh_2(pfb)_4$	31	26:74
$Rh_2(OAc)_4$	84	29:71
$Rh_2(cap)_4$	71	30:70



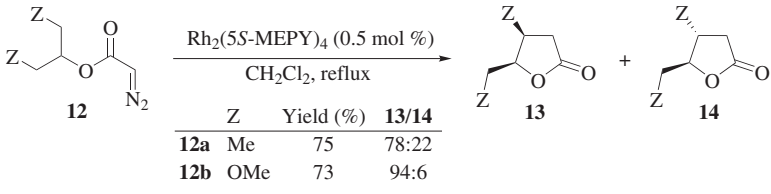
Catalyst	Yield (%)	**10/11**
$Rh_2(pfb)_4$	75	34:66
$Rh_2(OAc)_4$	84	75:25
$Rh_2(cap)_4$	80	92:8

(Eq. 8)



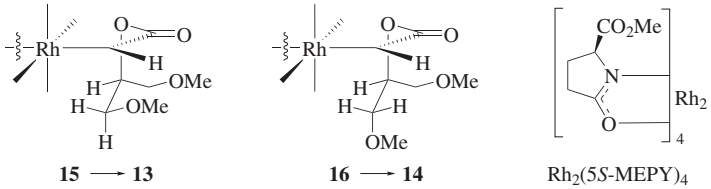
Intramolecular C–H insertion generally provides five-membered ring products; however, exceptions do exist. Conformational and electronic effects, coupled with catalyst selection, result in the predominant formation of four-membered rings in a number of instances,[95,134,135,143,144] and insertion to form a three-membered ring has been observed in one case.[145] The formation of six-membered rings is comparatively rare, although several examples exist in which six-membered rings are the exclusive C–H insertion products.[134,146–148] Other ring sizes have also been observed as C–H insertion products, however rarely, and stereocontrol is negligible.[40,145,149–151] Conformational preferences can lead to interesting selectivities; an example is a comparison of results from catalytic asymmetric C–H insertion reactions with 3-pentyl diazoacetate (**12a**)[152] and those with 1,3-dimethoxy-2-propyl diazoacetate (**12b**) (Eq. 9).[153,154] Diastereoselectivity is significantly higher in the latter reaction than in the former. This increase in diastereoselectivity has been proposed to arise from conformational preferences due to steric and/or dipolar interactions between the polar face of the catalyst and an alkoxy group of the intermediate rhodium-bound carbene.[153] According to this

model, conformer **15** minimizes repulsive dipolar interactions between the alkoxy group and the heteroatoms of the catalyst face, providing the major diastereomer **13**. Conformer **16**, in which the polar catalyst face and an alkoxy group are proximal, generates the minor diastereomer **14**. This electronic control of conformational preferences in the transition states of **15** vs. **16** obviates the need for further catalyst ligand control that is required by 3-pentyl diazoacetate to obtain high diastereoselectivity. The electronic influence of dirhodium ligands on stereoselectivity follows the expected pattern, that is, the less electron-withdrawing the ligands, the higher the stereoselectivity.[56,105]

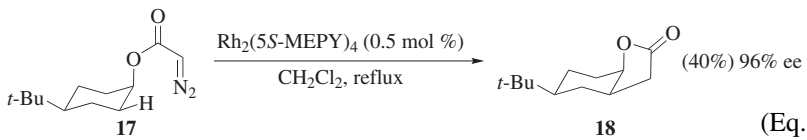


	Z	Yield (%)	**13/14**
12a	Me	75	78:22
12b	OMe	73	94:6

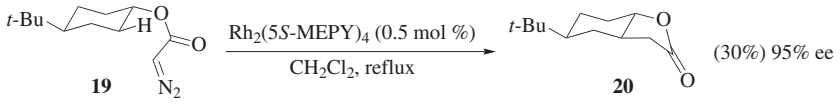
(Eq. 9)



Reactions of conformationally biased 4-*tert*-butylcyclohexyl diazoacetates provide an understanding of conformational influences on C−H insertion transition state geometries.[155] In *cis*-4-*tert*-butylcyclohexyl diazoacetate the diazoacetate unit (and resulting metal carbene) prefers an axial position, and the neighboring equatorial C−H bonds are more available for insertion. As expected, the *cis* isomer **17** gives exclusive formation of the *cis*-bicyclic lactone isomer **18** (Eq. 10). In contrast, with *trans*-4-*tert*-butylcyclohexyl diazoacetate (**19**) the intermediate metal carbene is restricted to an equatorial position from which both neighboring axial and equatorial C−H bonds are available for insertion, potentially leading to either or both *cis*- or *trans*-bicyclic lactones. In this case only the *trans*-bicyclic lactone isomer **20** is observed (Eq. 11).[155] Because the *trans*-bicyclic lactone is only the minor product in the C−H insertion reaction of unsubstituted cyclohexyl diazoacetate, the implication is that C−H insertion occurs preferentially into the equatorial C−H bond from an axial carbene-bearing substituent in conformationally mobile cyclohexyl diazoacetates. Similar results are reported for the 4-methylcyclohexyl diazoacetates.[155]

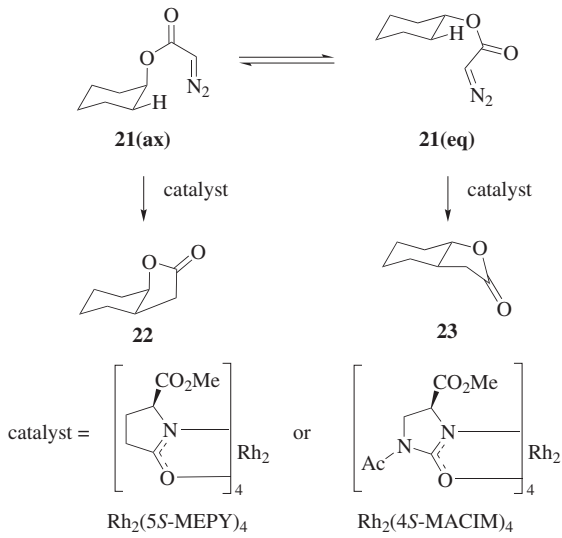


(Eq. 10)



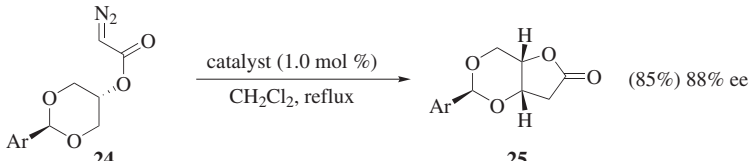
(Eq. 11)

Support for the hypothesis that insertion of the carbene in cyclohexyl systems occurs preferentially from the substituent occupying the axial position is provided by a theoretical study of diastereoselective C–H insertion reactions.[126] Using density functional theory (DFT) calculations, transition-state structures of axial or equatorial C–H insertion processes from the reaction of cyclohexyl diazoacetate **21** with $Rh_2(5S\text{-MEPY})_4$ or $Rh_2(4S\text{-MACIM})_4$ have been evaluated (Scheme 3). The lowest-energy transition structure found for this reaction stems from the carbene-bearing substituent occupying an axial position (**21ax**), allowing insertion only into the equatorial C–H bond to generate **22**. The second-lowest energy transition structure is predicted to stem from insertion of an equatorial carbene-bearing substituent (**21eq**) into the neighboring equatorial C–H bond, giving rise to **23**. This analysis is consistent with the outcome of the catalytic reaction of 4-substituted cyclohexyl diazoacetates; when the carbene-bearing substituent is forced to occupy the equatorial position, insertion also occurs into the neighboring equatorial C–H bond, yielding the *trans* isomer. Calculations of the relative transition-state energies confirm that the energy difference between the transition states leading to **22** *vs.* **23** is substantially greater with the catalyst $Rh_2(4S\text{-MACIM})_4$ than with $Rh_2(5S\text{-MEPY})_4$ (Scheme 3), and this is in line with observed selectivities.[42]

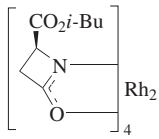


Scheme 3

A departure from the conformational model used with cyclohexyl diazoacetates is observed with 2-aryl-1,3-dioxan-5-yl diazoacetates **24** (Eq. 12).[154] Intramolecular cyclization provides the *cis* isomer **25** exclusively, as opposed to the expected *trans* isomer. In the previously discussed six-membered ring system, the six-membered ring is assumed to adopt the chair conformation. Anomeric effects of the two oxygen atoms on the α-hydrogen atoms undergoing the insertion are likely responsible for the observed selectivity. Use of the 2-naphthyl derivative provides convenient access to the 2-naphthyl-substituted 2-deoxyribono-1,4-lactone in good yield and excellent diastereo- and enantioselectivity.



Ar	Catalyst	Yield (%)	% ee
Ph	Rh_2(4*S*-IBAZ)$_4$	85	88
2-naphthyl	Rh_2(5*S*-MEPY)$_4$	72	95



Rh_2(4*S*-IBAZ)$_4$

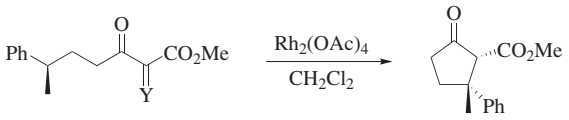
(Eq. 12)

SCOPE AND LIMITATIONS

Preparation and Stability of Metal Carbene Precursors

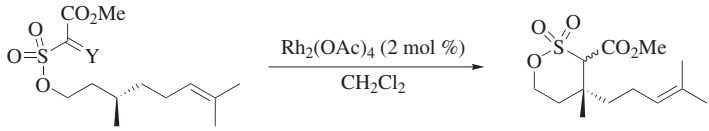
The synthetic utility of diazocarbonyl compounds has prompted the development of several practical means of introducing the diazo functionality into substrates. Described in this section are some of the more commonly used protocols for the preparation of α-diazocarbonyl compounds; previous reviews should be consulted for a more comprehensive description of this chemistry.[32,40,71–73,156–158] In situ methods[159] are also available, but they are subject to the limitations of the method that is employed.[81,156,160] *N*-Sulfonyl-1,2,3-triazoles are promising alternatives to diazocarbonyl compounds for metal carbene reactions,[161,162] but applications in C–H insertion reactions have not yet been reported.

A comparison of the reactivity of carbenes generated from iodonium ylides with that of the corresponding diazocarbonyl compounds shows no apparent advantage in the use of iodonium ylides other than the avoidance of the potentially explosive diazo compounds; results from both carbene precursors typically parallel each other.[45,83–86,163–168] Because no advantage accrues from the use of iodonium ylides in the few examples reported (e.g., Eq. 13–14),[86,169] and because the reactivity of iodonium ylides has been reviewed,[45] this chapter does not discuss these metal-carbene precursors further.



(Eq. 13)

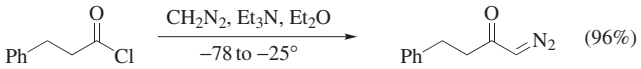
Y	Yield (%)	Temp	Time
N_2	59	rt	30 min
IPh	57	0°	3 h



(Eq. 14)

Y	Yield (%)	Conditions
N_2	84	40°
H_2	52	PhI=O, Cs_2CO_3, 3 Å MS

Diazo ketones having the general structure $RCOCHN_2$ are synthesized by addition of an acyl chloride or mixed carbonic anhydride to an ethereal solution of diazomethane.[170] The hydrochloric acid evolved in the course of this reaction is scavenged by an excess of diazomethane or by triethylamine (Eq. 15).[170] Methods for the generation of diazomethane have been described in considerable detail;[171–173] the most commonly used reagent is the commercially available Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide).[173] Commercially available trimethylsilyldiazomethane may be used as a safer substitute for diazomethane.[174–176] Homologs of diazomethane can also be acylated to form $RCOC(N_2)R'$, although the reaction of higher diazoalkanes is often inefficient.[177–198]

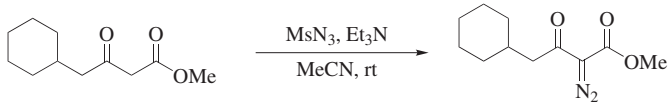


(Eq. 15)

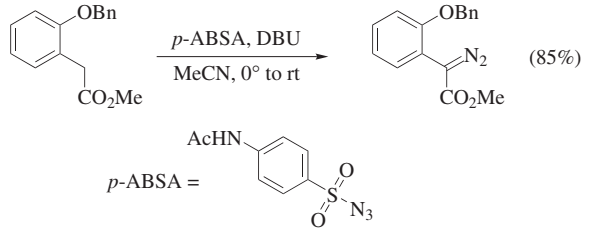
Diazo transfer between an enolate and a sulfonyl azide is used to access a wide range of α-diazocarbonyl compounds.[32,40,71] The scope and limitations of this reaction have been described in several reviews[32,40,71] and will be only briefly mentioned here. The thermal stability of sulfonyl azides, a large number of which have been evaluated for their synthetic utility and safety characteristics,[32,199–202] can be a significant limitation of this method in large-scale preparations. Several of these azides have been designed to optimize diazo transfer, to reduce the explosion hazard, or to ease the separation of the product sulfonamide from the diazocarbonyl compound,[199,203–217] and a few of them are commercially available.

Diazo transfer to the α-position of a carbonyl group requires formation of an enolate anion; if the reacting methylene group is activated by only one carbonyl group, a strong base is required. However, if the use of strong bases such as

lithium diisopropylamide (LDA) results in the formation of side products, indirect methods can be employed. When the α-position of a carbonyl group is sufficiently acidic to allow deprotonation by an organic amine, direct diazo-transfer conditions are used. Moderately basic amines such as triethylamine or DBU (1,8-diazabicylclo[5.4.0]undec-7-ene) are typically employed. 1,3-Dicarbonyl compounds such as β-diketones, β-keto esters, and malonic esters are suitable for direct diazo transfer (Eq. 16);[199] an aryl or vinyl group also has an activating effect for diazo transfer (Eq. 17).[218]

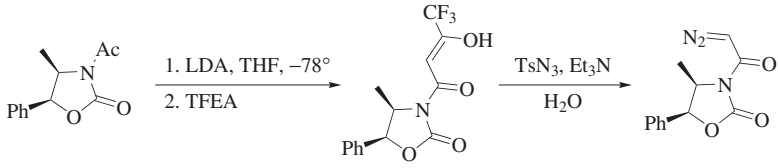


(Eq. 16)



(Eq. 17)

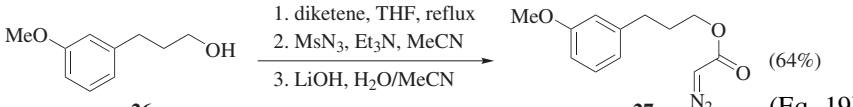
The Regitz deformylating diazo transfer protocol and its variants have found widespread application for diazo transfer to a methylene or methyl group that is not sufficiently acidic to be deprotonated by mild bases.[32,40,71] This process begins with a Claisen condensation of the carbonyl compound with ethyl formate.[72,73] The resulting 1,3-dicarbonyl compound is activated for diazo transfer, which occurs with subsequent deformylation (or deacylation). The formyl group is released as a sulfonamide (RSO_2NHCHO), which is usually easily separated from the diazocarbonyl product during workup due to its acidity. Variants of the Regitz conditions in which ethyl formate is replaced by TFEA (2,2,2-trifluoroethyl trifluoroacetate)[219–221] (Eq. 18) or benzoyl chloride[222] have also been developed, and in many cases provide yields that are markedly superior to those obtained via the original protocol.



(Eq. 18)

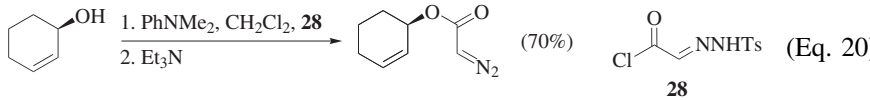
α-Diazo-β-keto esters or amides can be subjected to base-promoted acyl cleavage to generate α-diazoacetates or α-diazoacetamides. Deacylation using an alkali metal hydroxide is frequently employed for the synthesis of diazoacetates such as **27** (Eq. 19).[223] In the complete process, alcohol **26** is treated with diketene

to form a β-keto ester. Reaction with mesyl azide and triethylamine generates the α-diazo-β-keto ester. Strong aqueous base cleaves the acyl group providing diazoacetate **27**.

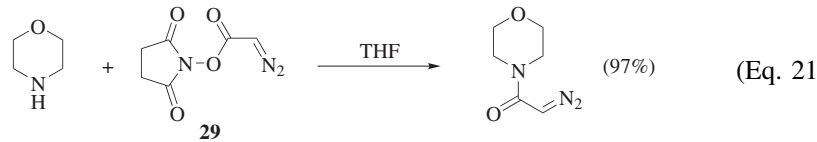


26 **27** (Eq. 19)

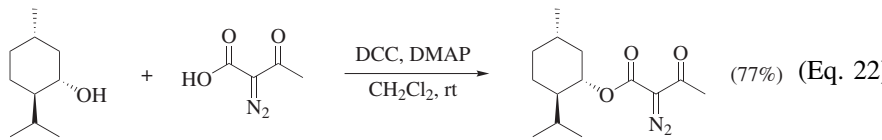
Direct diazoacetylation of alcohols and amines provides a convenient means of accessing α-diazoacetates (Eq. 20)[224] and α-diazoacetamides (Eq. 21).[225] 2-(2-Tosylhydrazono)acetyl chloride (**28**)[226,227] is an effective reagent for the synthesis of α-diazoacetates (Eq. 20). Succinimidyl diazoacetate **29** selectively transfers the acyldiazo moiety to amines and phenols (but not alcohols) under mild conditions (Eq. 21); two preparations of **29** have been reported,[225,228] but only the latter[228] has been found to be routinely reproducible in good yield. A method of preparing α-diazoacetoacetates by the direct coupling of 2-diazoacetoacetic acid and an alcohol using DCC and a catalytic amount of DMAP has recently been reported (Eq. 22).[77] Diazoacetoacetic acid is synthesized by hydrogenolysis of benzyl diazoacetoacetate catalyzed by Pd/C.[77] The main advantage of this method is that base-sensitive substrates are tolerated, thus enabling the production of diazo compounds that are difficult to make by common methods.



28 (Eq. 20)

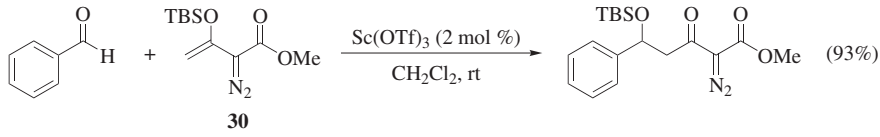


29 (Eq. 21)

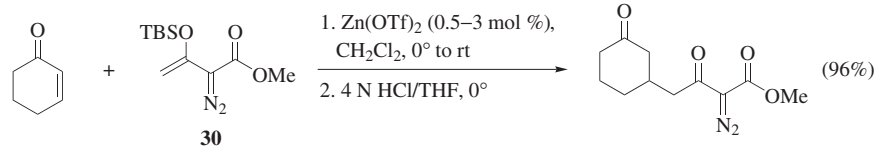


(Eq. 22)

Silyl enol ether **30** undergoes both Mukaiyama aldol (Eq. 23)[79] and Mukaiyama–Michael (Eq. 24)[75] addition reactions with aldehydes and ketones catalyzed by a variety of Lewis acids, the most general and economical being zinc(II) triflate.[75,229] In turn, **30** is prepared from methyl α-diazoacetoacetate.[230,231] The products of these reactions are functionalized β-keto-α-diazoacetate esters. Ag(I)-BINAP catalysts have been used to produce enantio-enriched β-keto-α-diazoacetate esters via the Mukaiyama aldol reaction.[232] Other methods involving acid- or base-promoted reactions have also been reported.[78,80,233–241]



(Eq. 23)



(Eq. 24)

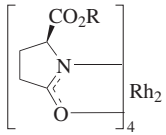
Survey of Catalysts

(Note: *The definitions of the abbreviations and acronyms used in the names of dirhodium catalysts are included in a list preceding the "Tabular Survey". There are also five Charts preceding the tables that depict all the catalysts used therein. Note, however, that the bold numbers assigned to these structures and used in the tables differ from those assigned and used in the text.*

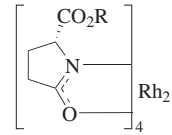
The selection of structures shown in Figs. 3–6 is intended to be representative of those that are described in this text. For a complete listing of catalysts, consult Charts 1–5.)

Chiral dirhodium(II) carboxamidate catalysts have emerged as excellent catalysts in intramolecular C–H insertion used for the synthesis of lactones and lactams.[43,69,70] The chiral dirhodium carboxamidate catalysts (e.g., **31**–**38**, Fig. 3) that are the most widely applicable in C–H insertion reactions are prepared from rhodium acetate and enantiomerically pure amino-acid-derived lactams, carbamates, or imides with a pendant ester that serves as the stereodirecting moiety.[69] Both amino acid enantiomers are available, although the natural (*S*)-enantiomer is accessible at lower cost. The $Rh_2(MEPY)_4$ catalysts (**31a** and **32a**)[55] were the first effective chiral dirhodium(II) carboxamidate catalysts to be prepared, and they have enjoyed widespread application in asymmetric C–H insertion reactions. However, the use of *N*-acylimidazolidinone (**35a**–**d** and **36a**–**d**)[223,242–244] as the chiral carboxamidate ligands gives significantly enhanced selectivities. The azetidinone-ligated catalysts **37a**–**d** and **38a**–**d**, whose OCN bite angles lengthen the rhodium–rhodium bonds, are more active than are dirhodium carboxamidate catalysts formed from five-membered ring lactams.[245,246] The pendant CO_2R group of these catalysts is necessary for high enantiocontrol. With increased steric congestion (for example, in 1- and 2-adamantyl diazoacetates) the $Rh_2(MEOX)_4$ catalysts (**33a** and **34a**) can provide higher levels of enantiocontrol than the $Rh_2(MEPY)_4$ catalysts (**31a** and **32a**).[247] This result is due in part to the more open nature of the catalyst face in oxazolidinate **33**, compared to pyrrolidinate (**31**)- or imidazolidinate (**35**)-ligated catalysts.

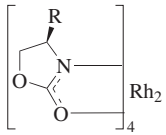
Chiral dirhodium(II) carboxylates (e.g., **39**–**48**, Fig. 4), of which the prolinate-based catalysts **39**[25,54,146,248] are the most effective in intermolecular reactions that



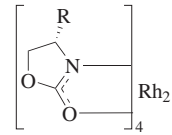
	R	
31a	Me	Rh_2(5*S*-MEPY)$_4$
31b	*t*-$BuCH_2$	Rh_2(5*S*-NEPY)$_4$
31c	*n*-$C_{18}H_{37}$	Rh_2(5*S*-ODPY)$_4$



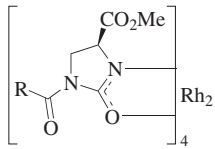
	R	
32a	Me	Rh_2(5*R*-MEPY)$_4$
32b	*t*-$BuCH_2$	Rh_2(5*R*-NEPY)$_4$
32c	*n*-$C_{18}H_{37}$	Rh_2(5*R*-ODPY)$_4$



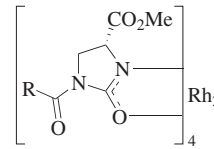
	R	
33a	MeO_2C	Rh_2(4*S*-MEOX)$_4$
33b	Ph	Rh_2(4*R*-PHOX)$_4$
33c	Bn	Rh_2(4*R*-BNOX)$_4$



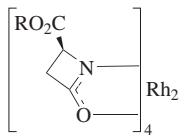
	R	
34a	MeO_2C	Rh_2(4*R*-MEOX)$_4$
34b	Ph	Rh_2(4*S*-PHOX)$_4$
34c	Bn	Rh_2(4*S*-BNOX)$_4$



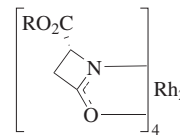
	R	
35a	Me	Rh_2(4*S*-MACIM)$_4$
35b	$BnCH_2$	Rh_2(4*S*-MPPIM)$_4$
35c	*c*-$C_6H_{11}CH_2$	Rh_2(4*S*-MCHIM)$_4$
35d	Ph	Rh_2(4*S*-MBOIM)$_4$



	R	
36a	Me	Rh_2(4*R*-MACIM)$_4$
36b	$BnCH_2$	Rh_2(4*R*-MPPIM)$_4$
36c	*c*-$C_6H_{11}CH_2$	Rh_2(4*R*-MCHIM)$_4$
36d	Ph	Rh_2(4*R*-MBOIM)$_4$



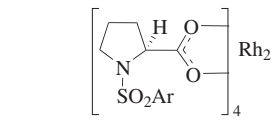
	R	
37a	Me	Rh_2(4*S*-MEAZ)$_4$
37b	*i*-Bu	Rh_2(4*S*-IBAZ)$_4$
37c	*c*-C_6H_{11}	Rh_2(4*S*-CHAZ)$_4$
37d	Bn	Rh_2(4*S*-BNAZ)$_4$
37e	*t*-$BuCH_2$	Rh_2(4*S*-NEPAZ)$_4$



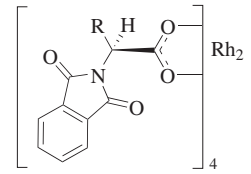
	R	
38a	Me	Rh_2(4*R*-MEAZ)$_4$
38b	*i*-Bu	Rh_2(4*R*-IBAZ)$_4$
38c	*c*-C_6H_{11}	Rh_2(4*R*-CHAZ)$_4$
38d	Bn	Rh_2(4*R*-BNAZ)$_4$
38e	*t*-$BuCH_2$	Rh_2(4*R*-NEPAZ)$_4$

Figure 3. Chiral dirhodium(II) carboxamidate catalysts.

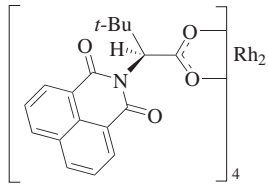
occur with vinyl- and aryldiazoacetates, have only rarely approached the selectivities obtained with chiral dirhodium(II) carboxamidate catalysts in the formation of lactones from diazoacetates.[143] However, chiral phthalimide-substituted amino acid ligands for dirhodium(II) (e.g., **40a–e**) are now recognized as effective alternatives to chiral carboxamidate ligands for highly enantioselective C–H insertion reactions in selected cases.[249,250]



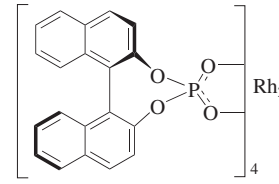
	Ar	
39a	Ph	Rh_2(*S*-BSP)$_4$
39b	4-*t*-BuC_6H_4	Rh_2(*S*-TBSP)$_4$
39c	4-*n*-$C_{12}H_{25}C_6H_4$	Rh_2(*S*-DOSP)$_4$
39d	1-Np	



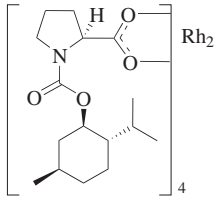
	R	
40a	Me	Rh_2(*S*-PTA)$_4$
40b	Bn	Rh_2(*S*-PTPA)$_4$
40c	*i*-Pr	Rh_2(*S*-PTV)$_4$
40d	*t*-Bu	Rh_2(*S*-PTTL)$_4$
40e	1-Ad	Rh_2(*S*-PTAD)$_4$



41 Rh_2(*S*-NTTL)$_4$



42 Rh_2(*S*-BNP)$_4$



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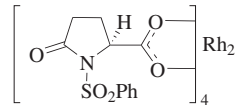

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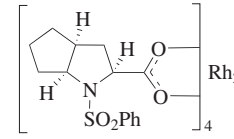

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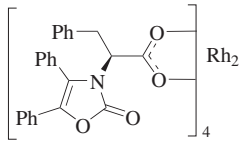

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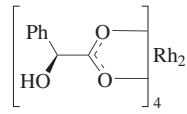
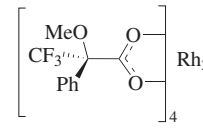


47 Rh_2(*S*-mandelate)$_4$

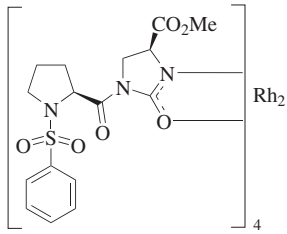


48

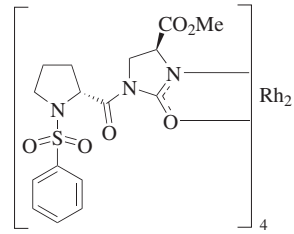
Figure 4. Chiral dirhodium(II) carboxylate catalysts.

Several other dirhodium *N*-acylimidazolidinone-ligated catalysts (Fig. 5) have been evaluated to determine the influence of multiple stereocenters in the ligands on reaction selectivity (**49** and **50**)[244] and the influence of size of the carboxylate group on reaction selectivity (**51** and **52**).[251] *cis*-Orthometalated arylphosphine dirhodium catalysts like **53** and **54**[252,253] (Fig. 6) appear to have unique capabilities for enantioselective C–H insertion reactions of diazo ketones for which dirhodium carboxamidates and carboxylates are unselective, but only a few examples are reported.[66,253]

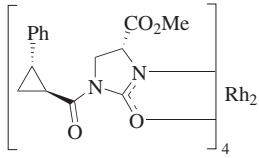
These dirhodium(II) complexes have two cisoid bridging carboxylates (O_2CR)[254] or imidates[255] and two ortho-metalated aryl phosphines (PC) for use as catalysts for C–H insertion reactions of diazo compounds. The *cis*-orthometalated



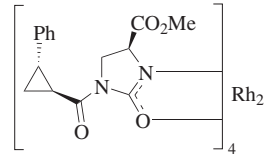
49a $Rh_2(4S,2'S\text{-BSPIM})_4$



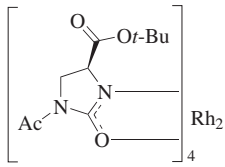
49b $Rh_2(4S,2'R\text{-BSPIM})_4$



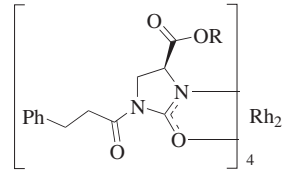
50a $Rh_2(4R,2'R,3'R\text{-MCPIM})_4$



50b $Rh_2(4S,2'R,3'R\text{-MCPIM})_4$

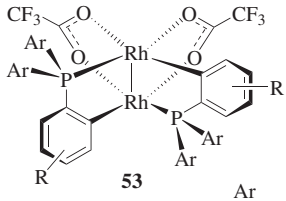


51 $Rh_2(4S\text{-BACIM})_4$



	R	
52a	Et	$Rh_2(4S\text{-EPPIM})_4$
52b	*t*-Bu	$Rh_2(4S\text{-BPPIM})_4$

Figure 5. Chiral dirhodium(II) *N*-acylimidazolidinone catalysts.



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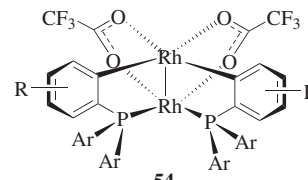


54

Ar	R
Ph	H
4-MeC_6H_4	4-Me
3-MeC_6H_4	3-Me
3,5-$Me_2C_6H_3$	3,5-Me_2
4-*t*-BuC_6H_4	*t*-Bu
4-FC_6H_4	F
3,5-$Me_2C_6H_3$	H

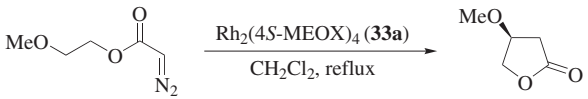
Figure 6. *cis*-Orthometalated arylphosphine dirhodium catalysts.

phosphines are oriented in a head-to-tail arrangement (**53**, Fig. 6) around the Rh_2^{4+} core or a *cis* head-to-head arrangement (**54**). The *cis*-orthometalated arylphosphine dirhodium catalysts **54** are achiral and show poor reactivity towards C–H insertion, but the isomeric complexes **53**, suitably resolved, can give both high reactivity and enantioselectivity in competitive C–H insertion reactions of selected diazo esters and diazo ketones.[66] Variation of the substituents on the metalated phenyl ring gives differences in enantioselectivity that are consistent with electronic influences on an electron-deficient carbene species. However, poor site selectivity can be a major drawback when using these catalysts.[66]

Synthesis of Lactones by C–H Insertion

The synthesis of lactones by catalytic, asymmetric, intramolecular C–H insertion performed with diazoacetates generally occurs with high enantiocontrol.[6,7,13,18,19,31,32,156] However, diazoacetoacetates and diazomalonates give lower enantioselectivities.[135,143,256,257] In the absence of steric or electronic constraints, γ-lactones are formed exclusively or predominantly. β-Lactone formation, which is facilitated by the electronic influence of the ester oxygen, is more common than is δ-lactone formation.

Monocyclic γ-Butyrolactones. 2-Methoxyethyl diazoacetate (**55**) (Eq. 25)[242,258] undergoes C–H insertion to give the lactone product in good yield and high enantiomeric excess with dirhodium carboxamidate catalysts **31**–**38**. Increasing the size of the alkoxy group lowers the enantioselectivity slightly, and steric crowding near the site of insertion does so dramatically. A more typical example is the reaction of 3-substituted-1-propyl diazoacetates[259] in which the advantage of chiral imidazolidinone-ligated $Rh_2(MPPIM)_4$ (**35b** and **36b**) catalysts relative to other chiral carboxamidate-derived dirhodium catalysts is demonstrated.



55 (Eq. 25)

These catalysts were also applied to the synthesis of lignan lactones (**56**)[259] and (*S*)-(+)-imperanene (**57**)[260] (Fig. 7). The imidazolidinone-based complexes **35a**,**b** and **36a**,**b** are the optimal catalysts for lactone formation, providing the highest levels of enantioselectivity. Without exception, the (*R*)-configured catalyst gives the (*R*)-configured product, and the (*S*)-configured catalyst gives the (*S*)-configured product. The amount of catalyst employed is 0.5 to 1.0 mol %, and yields of C–H insertion products are in the range of 55–80%.

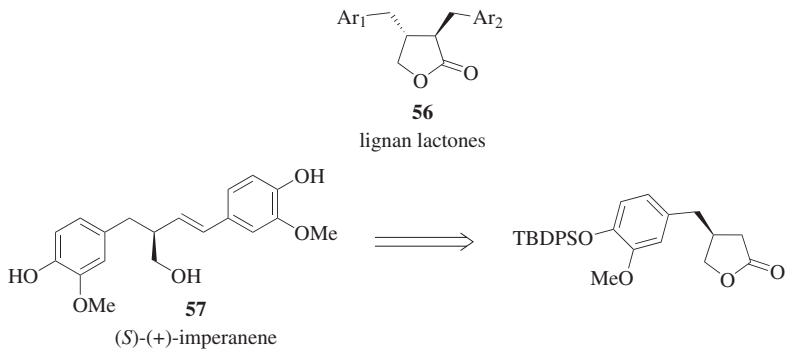
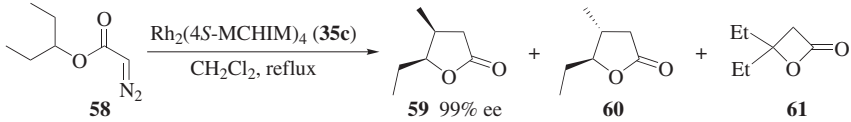


Figure 7. Lignan lactones and (*S*)-(+)-imperanene.

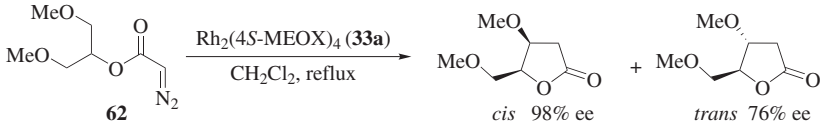
Desymmetrization of secondary alkyl diazoacetates (Eq. 26)[152] is an efficient strategy to access disubstituted γ-lactones with excellent diastereo- and enantioselectivities. Catalytic diazo decomposition reactions of 3-pentyl diazoacetate (**58**) produce three isomers, the two γ-lactone diastereomers **59** and **60**, and β-lactone **61** (arising from carbene insertion into the ether-oxygen-activated methine C–H bond). Of the catalysts examined, Rh_2(4*S*-MCHIM)$_4$ (**35c**) gives the highest diastereocontrol and provides the *cis*-disubstituted γ-lactone **59** in 99% ee.



59 + **60** + **61** (90%), **59/60/61** = 95:2:3

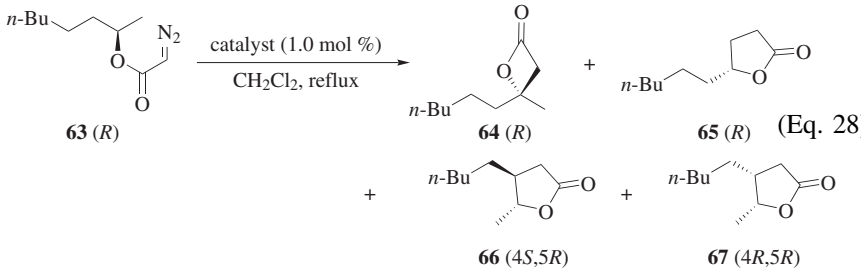
(Eq. 26)

Desymmetrization of 1,3-methoxy-2-propyl diazoacetate (**62**) is applied to the synthesis of deoxyxylolactone derivatives in high yield and with excellent enantio- and stereoselectivity favoring the *cis* isomer (Eq. 27).[153,154] Reactions of (*R*)-2-octyl diazoacetate (**63**) show match/mismatch catalyst influences with chiral dirhodium carboxamidates (Eq. 28).[134] The β-lactone product **64** resulting from the mismatch of catalyst and diazoacetate configurations is dominant among the products **64**–**67**.



cis + *trans* (—), *cis*/*trans* = 91:9

(Eq. 27)

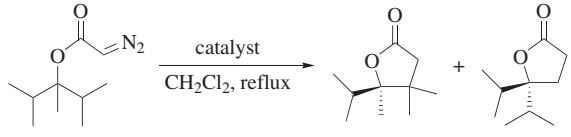


63 (*R*) **64** (*R*) **65** (*R*) (Eq. 28)

66 (4*S*,5*R*) **67** (4*R*,5*R*)

Catalyst	**64–67** Yield (%)	**64/65/66/67**
Rh_2(5*S*-MEPY)$_4$ (**31a**)	59	66:14:14:6
Rh_2(5*R*-MEPY)$_4$ (**32a**)	53	43:1:14:42
Rh_2(4*S*-MEOX)$_4$ (**33a**)	59	83:10:4:3
Rh_2(4*R*-MEOX)$_4$ (**34a**)	71	57:2:12:29

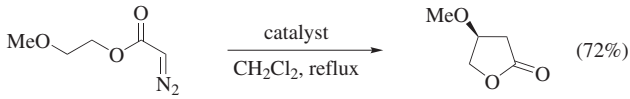
With tertiary diazoacetates, such as **68**, where access to a methyl group as well as to a secondary or tertiary C–H bond for insertion is possible, site selectivity becomes an issue.[261] Not enough data are available to allow the derivation of general rules on such selectivity (Eq. 29).[258] Chiral catalysts developed after 1995 (e.g. **35b** and **37**) have not yet been applied to these more complex substrates.



68 **69** **70** (Eq. 29)

Catalyst	**69** + **70** Yield (%)	**69/70**	% ee **70**
Rh_2(5*S*-MEPY)$_4$ (**31a**)	66	70:30	61
Rh_2(4*S*-MEOX)$_4$ (**33a**)	70	93:7	0
Rh_2(4*S*-MACIM)$_4$ (**35a**)	73	83:17	85

Significant match/mismatch effects on enantioselectivity are often observed in the C–H insertion reactions: substrate **55**, already illustrated in Eq. 25, provides a dramatic example (Eq. 30).[244]

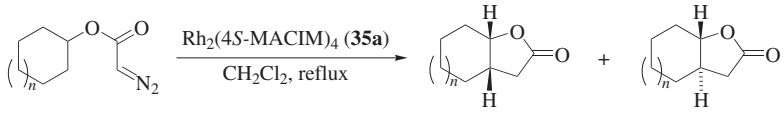


55 (Eq. 30)

Catalyst	% ee
Rh_2(4*S*,2′*S*-BSPIM)$_4$ (**49a**)	94
Rh_2(4*S*,2′*R*-BSPIM)$_4$ (**49b**)	6

Bicyclic γ-Butyrolactones. Chiral dirhodium(II) carboxamidates exhibit exceptional enantio- and diastereoselectivities for C–H insertion reactions of

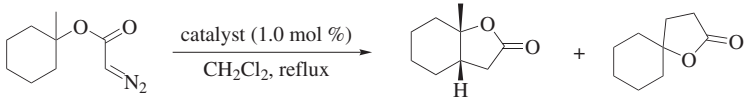
cycloalkyl diazoacetates. Cycloalkyl diazoacetates **71** ($n = 1 - 3$) have been used extensively to evaluate diastereo- and enantioselectivities provided by dirhodium catalysts (Eq. 31).[155,242–244,251,262–264] With the exception of the reactions with cyclopentyl diazoacetate, the catalysts $Rh_2(4S\text{-MEOX})_4$ (**33a**) and $Rh_2(5S\text{-MEPY})_4$ (**31a**) show high enantioselectivities, but the lactone products are formed with low diastereoselectivity.[155,243] Only with the imidazolidinone-ligated catalyst $Rh_2(4S\text{-MACIM})_4$ (**35a**) were high diastereo- and enantioselectivities first achieved,[243] as illustrated by the predominance of lactone **72** over its isomer **73**. A later report shows that $Rh_2(4S\text{-MPPIM})_4$ (**35b**) provides comparable or, in some cases, even higher selectivities.[244]



71 **72** **73** (Eq. 31)

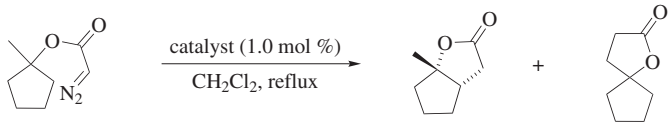
n	**72** + **73** Yield (%)	**72/73**	% ee **72**
1	70	99:1	97
2	75	99:1	96
3	62	99:1	97

Intramolecular C–H insertion reactions of diazoacetates from cyclic, tertiary alcohols produce bicyclic lactones with lower enantioselectivities than corresponding reactions with their secondary counterparts.[261] Also, insertion into a methyl C–H bond is competitive with insertion into a secondary C–H bond. Reactions of 1-methylcyclohexyl diazoacetate (**74**) and 1-methylcyclopentyl diazoacetate (**77**) exhibit slightly higher site selectivities with $Rh_2(4S\text{-MACIM})_4$ (**35a**) and $Rh_2(5S\text{-MEPY})_4$ (**31a**) than with the more open $Rh_2(4S\text{-MEOX})_4$ (**33a**) (Eqs. 32 and 33),[265] as determined from the ratios of the bicyclic γ-lactone products **75** and **78** to the spiro-products **76** and **79**.



74 **75** **76** (Eq. 32)

Catalyst	**75** + **76** Yield (%)	**75/76**	% ee **75**
$Rh_2(5S\text{-MEPY})_4$ (**31a**)	63	90:10	75
$Rh_2(4S\text{-MEOX})_4$ (**33a**)	60	78:22	40
$Rh_2(4S\text{-MACIM})_4$ (**35a**)	68	90:10	90
$Rh_2(4S\text{-BNOX})_4$ (**33c**)	30	—	44

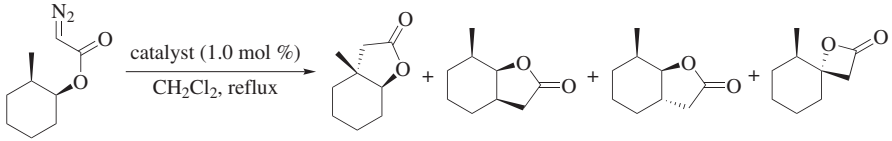


77 **78** **79**

(Eq. 33)

Catalyst	**78** + **79** Yield (%)	**78**/**79**	% ee **78**
Rh_2(5*S*-MEPY)$_4$ (**31a**)	52	94:6	36
Rh_2(4*S*-MEOX)$_4$ (**33a**)	61	83:17	33
Rh_2(4*S*-MACIM)$_4$ (**35a**)	56	90:10	85
Rh_2(4*S*-BNOX)$_4$ (**33c**)	17	—	1

Selectivity in C–H insertion reactions of chiral, non-racemic diazoacetates can be maximized using chiral catalysts, and is highly dependent upon the absolute configuration of the catalyst that is used. An excellent example of a match/mismatch effect is provided by the reactions of enantiomerically pure (1*S*,2*R*)-*cis*-2-methylcyclohexyl diazoacetate (**80**) and its enantiomer (1*R*,2*S*)-*cis*-2-methylcyclohexyl diazoacetate catalyzed by each enantiomer of Rh_2(MEPY)$_4$ (**31a** and **32a**), Rh_2(MEOX)$_4$ (**33a** and **34a**), and Rh_2(MPPIM)$_4$ (**35b** and **36b**) species (Eq. 34).[134] With Rh_2(4*S*-MPPIM)$_4$ (**35b**), for example, low site selectivity is obtained, and the low yield (46%) suggests severe constraints to C–H insertion. Of the four insertion products **81**–**84**, three are obtained in appreciable amounts. In contrast, with Rh_2(4*R*-MPPIM)$_4$ (**36b**) C–H insertion of enantiomer **80** provides exceptionally high site selectivity and diastereoselectivity; product **82** is formed almost exclusively. The outcome from reactions of enantiomer **80** with the more open Rh_2(MEOX)$_4$ catalysts is different: the "mismatched" (4*S*)-catalyst (**33a**) forms product **81** with very high selectivity whereas the "matched" (4*R*)-catalyst (**34a**) forms products **82** and **83** with high site selectivity but, typical for this catalyst, only fair diastereoselectivity (~12:1). Similar results are obtained with the Rh_2(MEPY)$_4$ catalysts, and mirror image results are obtained with (1*R*,2*S*)-*cis*-2-methylcyclohexyl diazoacetate (*ent*-**80**) with each set of catalysts. The formation of β-lactone **84** is particularly illustrative of the configurational mismatch between catalyst and substrate;

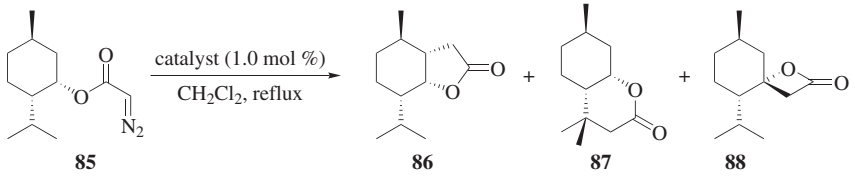


80 **81** **82** **83** **84**

Catalyst	**81**–**84** Yield (%)	**81**/**82**/**83**/**84**
Rh_2(5*S*-MEPY)$_4$ (**31a**)	95	94:1:0:5
Rh_2(5*R*-MEPY)$_4$ (**32a**)	79	4:91:3:2
Rh_2(4*S*-MEOX)$_4$ (**33a**)	82	90:1:0:9
Rh_2(4*R*-MEOX)$_4$ (**34a**)	91	2:88:7:3
Rh_2(4*S*-MPPIM)$_4$ (**35b**)	46	28:16:0:56
Rh_2(4*R*-MPPIM)$_4$ (**36b**)	88	0:98:0:2

(Eq. 34)

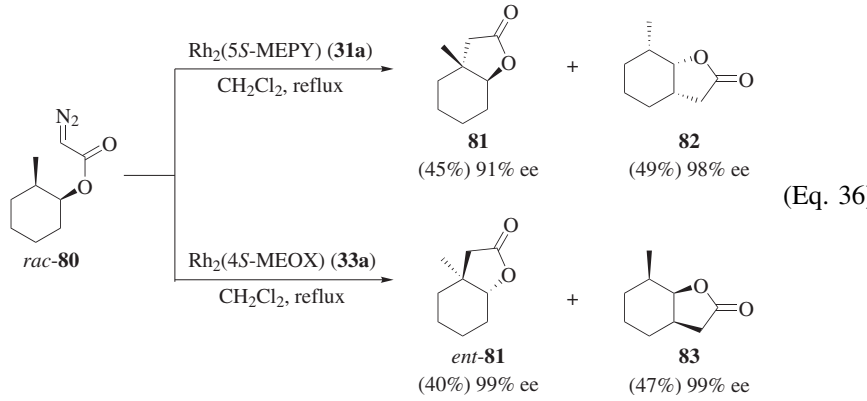
however, β-lactone formation is only rarely observed with diazoacetates.[40,135,143] The insertion products **86–88** resulting from reactions with the single enantiomer of D-(+)-menthyl diazoacetate **85** also show match/mismatch influences with enantiomeric sets of chiral dirhodium carboxamidate catalysts (Eq. 35).[134]



Catalyst	**86–87** Yield (%)	**86/87/88**
Rh_2(5*S*-MEPY)$_4$ (**31a**)	65	52:45:3
Rh_2(5*R*-MEPY)$_4$ (**32a**)	75	89:11:0
Rh_2(4*S*-MEOX)$_4$ (**33a**)	77	28:39:33
Rh_2(4*R*-MEOX)$_4$ (**34a**)	97	98:2:0

(Eq. 35)

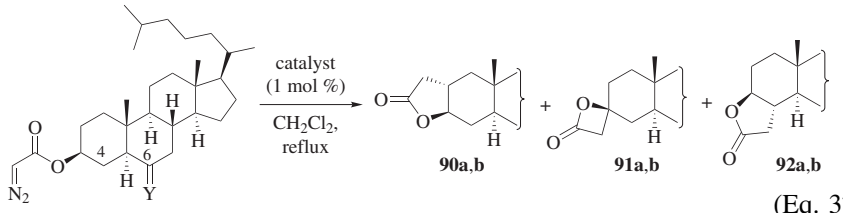
The high degree of control that catalyst configuration has over product distribution of chiral diazoacetates is further illustrated by the kinetic resolution of racemic mixtures of methyl-substituted cyclohexyl diazoacetates.[134] Results obtained with *rac-cis*-2-methylcyclohexyl diazoacetate (**80**) confirm that Rh_2(5*S*-MEPY)$_4$ (**31a**) directs intramolecular C–H insertion of the (1*S*,2*R*)-enantiomer to **81** (91% ee, 45% yield) and the (1*R*,2*S*)-enantiomer to **82** (98% ee, 49% yield) with high selectivity (Eq. 36).[266] With catalyst Rh_2(4*S*-MEOX)$_4$ (**33a**) *rac-cis*-2-methylcyclohexyl diazoacetate produces instead the (1*R*,2*S*) enantiomer *ent*-**81** whereas the (1*S*,2*R*) enantiomer produces **83** (Eq. 36).



(Eq. 36)

Steroidal Lactones. The conformationally rigid 5α-cholestan-3β-yl diazoacetate (**89a**) and 6-keto-5α-cholestan-3β-yl diazoacetate (**89b**) undergo catalyst-controlled, intramolecular C–H insertion reactions that are markedly dependent on ligand structure and configuration (Eq. 37).[135] The (*R*)-configured ligands on dirhodium(II) favor attack at the equatorial C–H bond of the 2-position of the

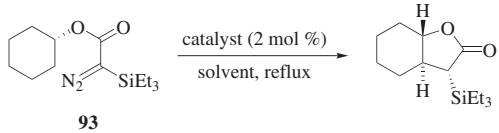
steroid to give **90a** and much less at the equatorial C–H bond of the 4-position to give **92a**; formation of β-lactone **91a** is a competing process but not the major reaction pathway. In contrast, lactone **91b** is a more significant product in reactions catalyzed by dirhodium carboxamidate catalysts whose ligands are in the (*S*)-configuration. The presence of a keto group in the 6-position of the steroid skeleton prevents C–H insertion at the 4-position.



(Eq. 37)

Y	Catalyst	**90–92** Yield (%)	**90/91/92**
H	Rh_2(5*R*-MEPY)$_4$ (**32a**)	89	72:20:8
H	Rh_2(5*S*-MEPY)$_4$ (**31a**)	87	6:62:32
H	Rh_2(4*R*-MEOX)$_4$ (**34a**)	86	60:33:7
H	Rh_2(4*S*-MEOX)$_4$ (**33a**)	91	4:70:26
O	Rh_2(5*R*-MEPY)$_4$ (**32a**)	85	61:39:0
O	Rh_2(5*S*-MEPY)$_4$ (**31a**)	76	8:92:0
O	Rh_2(4*R*-MEOX)$_4$ (**34a**)	88	43:57:0
O	Rh_2(4*S*-MEOX)$_4$ (**33a**)	90	3:97:0

Silylated γ-Butyrolactones. α-Silylated 1,4-lactones are produced in good yield and with moderate enantiocontrol when cyclohexyl diazo(triethylsilyl) acetates undergo diazo decomposition, and the highest enantioselectivities are achieved in reactions catalyzed by the modified imido-acid ligated Rh_2(*S*-NTTL)$_4$ (**41**) and similar chiral dirhodium(II) carboxylate catalysts (Eq. 38).[256] In contrast with diazoacetates without the silyl group, only insertion into the equatorial C–H bond is observed. The chiral dirhodium(II) carboxamidate catalysts are much less reactive toward C–H insertion with substrate **93** compared to dirhodium(II) carboxylate catalysts. Chiral prolinate-ligated complexes are also reactive, but provide low enantioselectivities. The chiral BINOL–phosphate ligated complexes Rh_2(BNP)$_4$ (**42** and its enantiomer) give only modest enantioselectivities. Diastereoselectivity is appreciably lower with the trimethylsilyl or triisopropylsilyl groups in place of triethylsilyl in substrate **93.**



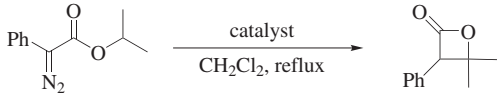
93

(Eq. 38)

Catalyst	Solvent	Yield (%)	% ee
$Rh_2(OAc)_4$	C_6H_6	61	—
Rh_2(5*S*-MEPY)$_4$ (**31a**)	C_6H_6	16	0
Rh_2(*S*-NTTL)$_4$ (**41**)	CH_2Cl_2	87	56
Rh_2(*S*-BNP)$_4$ (**42**)	C_6H_6	30	40

β-Lactones. As is readily apparent from the examples discussed thus far, γ-lactones are nearly always the exclusive C–H insertion products of alkyl diazoacetates. β-Lactones are often minor products, and they are typically not reported. The exception is in C–H insertion reactions of 2-octyl diazoacetate, from which the corresponding β-lactone is the major product (see Eq. 28). When a substantial conformational bias exists, monosubstituted diazoacetates form β-lactones.[134,135,266] The utility of β-lactones in the synthesis of natural products and biologically active compounds makes them appealing targets.[268–271]

Alkyl phenyldiazoacetates produce β-lactones as the dominant or sole intramolecular C–H insertion products (Eq. 39).[143] Catalytic, intramolecular cyclization of isopropyl 2-diazo-2-phenylacetate (**94**) occurs by insertion into the methine C–H bond to yield β-lactone **95** with the γ-lactone arising from insertion into the methyl C–H bond as only a trace component, irrespective of the catalyst used. Enantioselectivities, however, are low (<40% ee). Note that the pyrrolidinone-, oxazolidinone-, or imidazolidinone-ligated dirhodium(II) carboxamidate catalysts (**31**–**36**) are relatively unreactive toward diazo decomposition of phenyldiazoacetates.

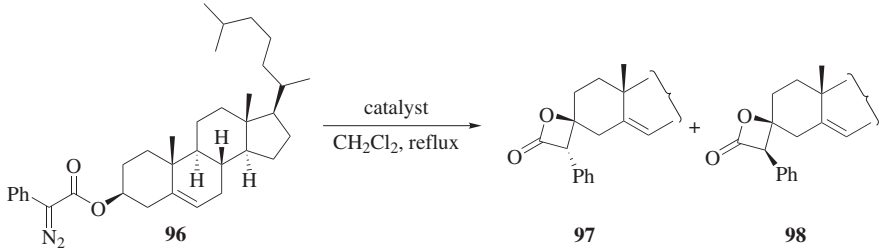


94 **95**

(Eq. 39)

Catalyst	Yield (%)	% ee
$Rh_2(OAc)_4$	84	—
Rh_2(*S*-DOSP)$_4$ (**39c**)	86	36
Rh_2(4*S*-MEAZ)$_4$ (**37a**)	83	33

Diastereoselectivities in β-lactone formation are modest in insertion reactions of chiral, non-racemic alkyl phenyldiazoacetates catalyzed by chiral dirhodium carboxamidates,[135,143] which exhibit matched/mismatched configurational effects as evidenced by the ratios of products **97** and **98** from steroid **96** (Eq. 40).



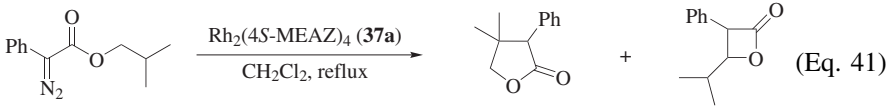
96 **97** **98**

Catalyst	**97** + **98** Yield (%)	**97/98**
Rh_2(4*S*-MEAZ)$_4$ (**37a**)	66	38:62
Rh_2(4*R*-MEAZ)$_4$ (**38a**)	69	16:84
Rh_2(*S*-DOSP)$_4$ (**39c**)	58	16:84

(Eq. 40)

In the phenyldiazoacetate systems that produce β-lactones, the methine C–H bond undergoing insertion[135,143] is electronically, but not sterically, more predisposed toward insertion than the neighboring methylene and methyl C–H bonds,

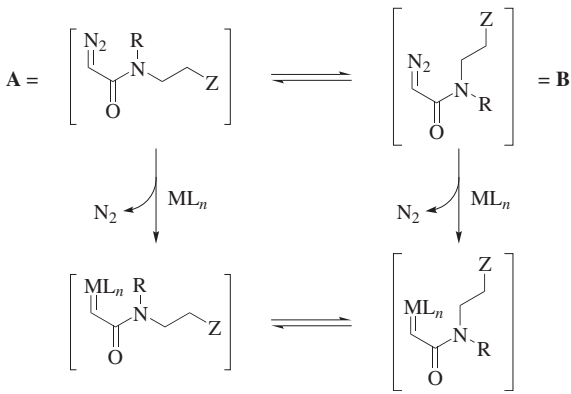
leading to γ-lactones.[120,272] The cyclization of substrate **99**, therefore, provides an interesting test on the limitations of β-lactone formation (Eq. 41).[143] To form a β-lactone in this case, insertion must occur into an oxygen-activated methylene rather than into an alkyl-group-activated methine C–H bond. Insertion occurs into the methine C–H to provide γ-lactone **100** to the exclusion of β-lactone **101**. This example suggests that β-lactone formation is suppressed if highly activated γ-C–H bonds are available.



99 **100** (94%) 90% ee **101** (0%) (Eq. 41)

Synthesis of Lactams by C–H Insertion

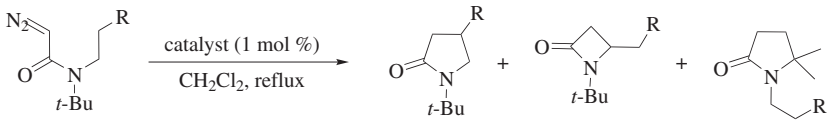
Lactams are obtained by the cyclization of metallo-carbenes generated from diazoacetamides, diazoacetoacetamides, and other functionalized diazoacetamides.[95] A wide range of carboxamidate- and carboxylate-ligated dirhodium complexes have been used to provide high stereoselectivities. Unlike the cyclization of diazoacetates to lactones, site selectivity in C–H insertion of diazoacetamides and diazoacetoacetamides is often complicated by the competition between the formation of β- and γ-lactams.[95,273] Whereas diazoacetates almost always produce γ-lactones, the amide nitrogen of diazoacetamides and their substituted counterparts strongly activate the adjacent C–H bond toward carbene insertion, giving rise to β-lactams. A major determinant of the reactivity and selectivity differences between diazoacetates and diazoacetamides is the barrier to rotation around the carbonyl–nitrogen bond, which is 17–22 kcal/mol for amides but only 10–12 kcal/mol for the carbonyl group of esters.[273a] Conformation **A** (Scheme 4) leads to an intermediate metallo-carbene in which the accessible C–H bond is far removed from the carbene center. Only in conformation **B** are the carbene center and C–H bond favorably disposed for insertion.



Scheme 4

The predominant presence of conformer **A** in diazo compounds derived from secondary amides explains why C–H insertion reactions with this class (R = H) are not synthetically viable processes. To promote rotation, and therefore C–H insertion, the nitrogen atom is usually protected with a bulky alkyl group (see below).

γ-Lactams and β-Lactams. The majority of asymmetric, intramolecular C–H insertion reactions of diazoacetamides use the dirhodium-carboxamidate-based catalysts **31**–**36**.[138,274] Modest enantioselectivities are obtained in the cyclization of *N*-*tert*-butyldiazoacetamides **102** (Eq. 42).[138] γ-Lactam formation (product **103**) is favored over carbene insertion into the C–H bond adjacent to nitrogen leading to β-lactam **104** by the presence of alkyl substituents. When the substituent R is an ethyl ether, β-lactam **104** is not observed. The electron-withdrawing character of an ester (R = CO_2Et) significantly inhibits the C–H insertions that lead to γ-lactam **103** and β-lactam **104**. Instead, the predominant cyclization pathway is carbene insertion into a methyl C–H bond of the *tert*-butyl protecting group to yield γ-lactam **105**. However, the use of Rh_2(4*S*-BNOX)$_4$ (**33c**) as the catalyst nearly completely blocks this side reaction, presumably because of the influence of the benzyl group of **33c** on regioselectivity. The *tert*-butyl protecting group is widely used because its methyl C–H bonds are generally unreactive toward carbene insertion,[95,273] but, as exemplified by Eq. 42, insertion into the *tert*-butyl group can occur if the *N*-alkyl C–H bonds are sufficiently deactivated.



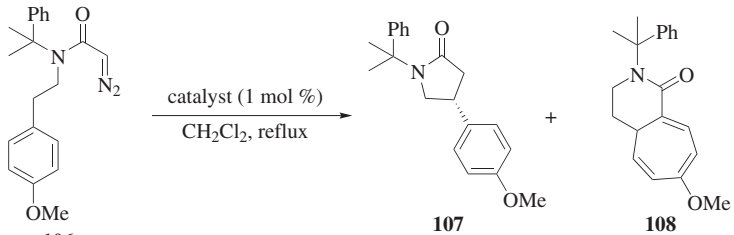
102 **103** **104** **105**

R	Catalyst	**103**–**105** Yield (%)	**103**/**104**/**105**	% ee **103**	% ee **104**
Et	Rh_2(4*S*-MEOX)$_4$ (**33a**)	82	91:9:0	71	80
i-Pr	Rh_2(4*S*-MEOX)$_4$ (**33a**)	93	82:18:0	69	65
EtO	Rh_2(4*S*-MEOX)$_4$ (**33a**)	97	100:0:0	78	—
EtO_2C	Rh_2(4*S*-MEOX)$_4$ (**33a**)	54	2:25:73	—	46
Et	Rh_2(5*S*-MEPY)$_4$ (**31a**)	74	88:12:0	63	73
i-Pr	Rh_2(5*S*-MEPY)$_4$ (**31a**)	91	80:20:0	58	72
EtO	Rh_2(5*S*-MEPY)$_4$ (**31a**)	91	100:0:0	58	—
EtO_2C	Rh_2(5*S*-MEPY)$_4$ (**31a**)	64	2:9:89	—	44
Et	Rh_2(4*S*-BNOX)$_4$ (**33c**)	92	92:8:0	<2	0
EtO_2C	Rh_2(4*S*-BNOX)$_4$ (**33c**)	54	12:88:<1	16	20

(Eq. 42)

Direct catalytic C–H insertion of diazoacetamide **106** using Rh_2(4*S*-MEOX)$_4$ (**33a**) as the catalyst produces γ-lactam **107** with high chemoselectivity (Eq. 43) but only modest enantioselectivity.[275] With other catalysts, including the more electrophilic chiral dirhodium carboxylates, formation of the product of carbene addition to the benzene ring (**108**) competes with C–H insertion; product yields

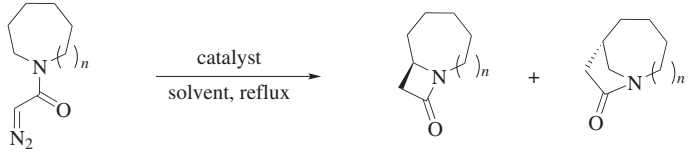
are low, and so is enantioselectivity. In this example, the *N*-cumyl group is found to be as effective as the *N*-*tert*-butyl group in establishing the amide conformation most suitable for C–H insertion, and this group can be more easily cleaved using trifluoroacetic acid.[276] Solvent and temperature in $Rh_2(4S\text{-MEOX})_4$-catalyzed reactions have negligible influence on yield and enantioselectivity.



106 **107** **108** (Eq. 43)

Catalyst	**107** + **108** Yield (%)	**107/108**	% ee **107**
$Rh_2(S\text{-DOSP})_4$ (**39c**)	36	47:53	3
$Rh_2(S\text{-NTTL})_4$ (**41**)	25	58:42	2
$Rh_2(5S\text{-MEPY})_4$ (**31a**)	53	87:13	18
$Rh_2(4S\text{-MEOX})_4$ (**33a**)	72	>98:2	47

The seven-membered-ring diazoacetamide **109a** undergoes intramolecular C–H insertion with excellent stereo- and site selectivity to provide β-lactam **110a** in 97% ee using the catalyst $Rh_2(5S\text{-MEPY})_4$ (**31a**, Eq. 44).[277] β-Lactam formation in diazo decomposition reactions of the eight-membered-ring diazoacetamide **109b** does not occur with high site selectivity, yielding both β- and γ-lactams in ratios that vary with both catalyst and temperature. Results from reactions in refluxing dichloromethane versus 1,2-dichloroethane show increased site selectivity for product **110** at higher temperature, which probably reflects higher conformational freedom. γ-Lactam **111b** is formed with an exceptionally high level of enantiocontrol.

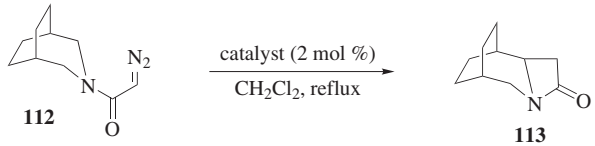


109 **110** **111** (Eq. 44)

a $n = 1$, **b** $n = 2$

n	Solvent	Catalyst	**110** + **111** Yield (%)	**110/111**	% ee **110**	% ee **111**
1	CH_2Cl_2	$Rh_2(5S\text{-MEPY})_4$ (**31a**)	67	>99:1	97	—
1	$C_2H_4Cl_2$	$Rh_2(4S\text{-MEOX})_4$ (**33a**)	68	99:1	92	—
2	CH_2Cl_2	$Rh_2(5S\text{-MEPY})_4$ (**31a**)	77	40:60	31	97
2	$C_2H_4Cl_2$	$Rh_2(5S\text{-MEPY})_4$ (**31a**)	67	67:33	30	96
2	CH_2Cl_2	$Rh_2(4S\text{-MEOX})_4$ (**33a**)	95	26:74	15	98
2	$C_2H_4Cl_2$	$Rh_2(4S\text{-MEOX})_4$ (**33a**)	68	49:51	8	96
2	$C_2H_4Cl_2$	$Rh_2(4S\text{-MACIM})_4$ (**35a**)	81	39:61	66 *ent*-**110**	96

The bicyclic 3-diazoacetyl-3-azabicyclo[3.2.2]nonane (**112**) undergoes C–H insertion to give the β-lactam **113** as the sole insertion product (Eq. 45).[277]

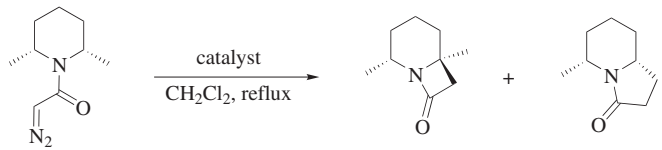


112 **113**

Catalyst	Yield (%)	% ee
Rh_2(5*S*-MEPY)$_4$ (**31a**)	70	96
Rh_2(4*S*-MEOX)$_4$ (**33a**)	81	93
Rh_2(4*S*-MACIM)$_4$ (**35a**)	—	<50

(Eq. 45)

Although 2,6-unsubstituted piperidines do not undergo C–H insertion, the desymmetrization of *cis*-2,6-dimethylpiperidine (**114**) provides the lactams **115** and **116** in good yields (Eq. 46).[277] Insertion into the methine C–H bond to form the β-lactam **115** is favored by a factor of ~8:1 over the γ-lactam **116**. In addition to the electronic factors favoring β-lactam formation—nitrogen activation of the adjacent C–H bond toward carbene insertion and preference for insertion into a methine over a methyl C–H bond—conformational factors also favor the formation of β-lactam **115**; the methyl substituents of substrate **114** likely occupy axial positions, which are not easily accessible to the metal-stabilized carbene.

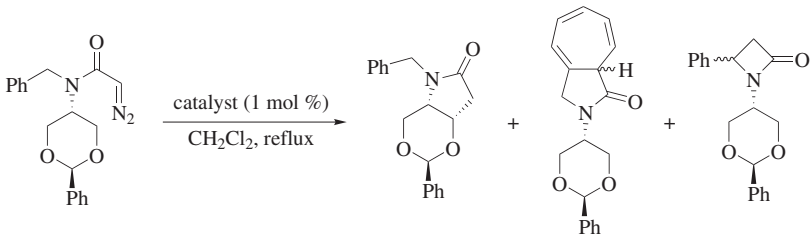


114 **115** **116**

Catalyst	**115** + **116** Yield (%)	**115**/**116**	% ee **115**
Rh_2(5*S*-MEPY)$_4$ (**31a**)	—	85:15	86
Rh_2(4*S*-MEOX)$_4$ (**33a**)	78	89:11	86
Rh_2(4*S*-MACIM)$_4$ (**35a**)	—	86:14	4

(Eq. 46)

Desymmetrization has also been successfully accomplished in C–H insertion reactions of 1,3-dioxan-5-yl diazoacetamide **117** bearing an *N*-benzyl group (Eq. 47).[278] In this case C–H insertion into a benzylic C–H bond (product **120**) and cyclization on the aryl group (product **119**) compete with the desired C–H insertion into the oxygen-activated C–H bond of the 1,3-dioxanyl ring (product **118**). The outcome of the dinitrogen extrusion performed with diazoacetamide **117** in refluxing dichloromethane is highly dependent on the catalyst used, and Rh_2(5*S*-MEPY)$_4$ (**31a**) provides the highest overall selectivities. Reactions performed in refluxing 1,2-dichloroethane are less site-selective. Carboxylate-ligated dirhodium catalysts (e.g. **39b**) favor aromatic substitution over C–H insertion in this case.

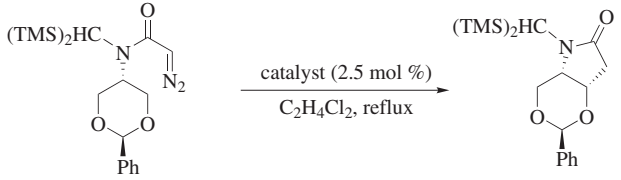


117 **118** **119** **120**

Catalyst	**118–120** Yield (%)	**118/119/120**	% ee **118**
$Rh_2(OAc)_4$	3	43:57:0	—
Rh_2(5*S*-MEPY)$_4$ (**31a**)	75	95:5:0	85
Rh_2(4*S*-MEOX)$_4$ (**33a**)	61	74:16:10	78
Rh_2(4*S*-IBAZ)$_4$ (**37b**)	45	49:35:16	19
Rh_2(4*S*-MPPIM)$_4$ (**35b**)	48	53:18:29	37
Rh_2(*S*-TBSP)$_4$ (**39b**)	9	22:78:0	56

(Eq. 47)

The use of the bis(trimethylsilyl)methyl group (BTMSM) to protect the nitrogen in diazo decomposition reactions of diazoacetamides[279,280] prevents the formation of byproducts that normally occur on the protective groups for nitrogen. Application to 1,3-dioxan-5-yl diazoacetamide **121** (an analog of **117**) gives the γ-butyrolactam C–H insertion product exclusively and in high yield (Eq. 48).[281] Although an incorrect rationale was provided for the stereoselectivities observed with enantiomeric catalysts due to impurities in the catalysts,[282] the influence of chiral carboxamidate-ligated catalysts is particularly revealing. The facts that Rh_2(MPPIM)$_4$ (**35b**) exerts no apparent enantiocontrol on reactions conducted in refluxing 1,2-dichloroethane, and that no reaction occurs in refluxing dichloromethane, suggest that a size limit exists in the operation of chiral carboxamidate-ligated dirhodium catalysts. The lack of selectivity in this C–H insertion may be due to reaction of a free carbene rather than a metallo-carbene.



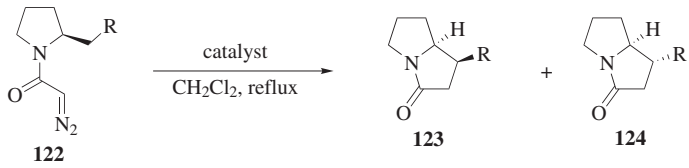
121

Catalyst	Yield (%)	% ee
Rh_2(5*S*-MEPY)$_4$ (**31a**)	82	44
Rh_2(4*S*-MEOX)$_4$ (**33a**)	94	90
Rh_2(4*S*-MEAZ)$_4$ (**37a**)	80	80
Rh_2(4*S*-MPPIM)$_4$ (**35b**)	48	1
Rh_2(S-PTTL)$_4$ (**40d**)	29	29

(Eq. 48)

High levels of diastereocontrol have been observed in reactions of chiral diazoacetamides with chiral catalysts. The chiral, non-racemic, proline-derived

diazoacetamide **122** undergoes C–H insertion with low diastereocontrol when achiral catalysts such as $Rh_2(OAc)_4$ are used. However, use of chiral dirhodium-carboxamidate catalysts provides lactam **123** in excellent yield and selectivity (Eq. 49);[283] β-lactam formation is not observed. Configurational match/mismatch is seen with the use of the two $Rh_2(MEPY)_4$ (**31a** and **32a**) enantiomers. Of particular significance in these examples is the high level of diastereoselectivity that favors the formation of lactam **123** over its configurationally more stable isomer **124**.



122 **123** **124** (Eq. 49)

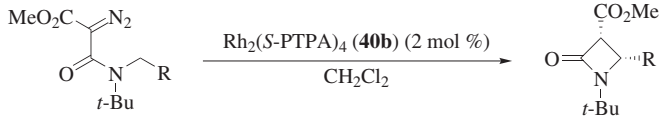
R	Catalyst	**122** + **123** Yield (%)	**123/124**
MeO	$Rh_2(OAc)_4$	45	53:47
MeO	$Rh_2(cap)_4$	45	63:37
MeO	Cu(OTf)	55	38:62
MeO	$Rh_2(5S\text{-MEPY})_4$ (**31a**)	95	90:10
MeO	$Rh_2(5R\text{-MEPY})_4$ (**32a**)	96	73:27
MeO	$Rh_2(4S\text{-MEOX})_4$ (**33a**)	99	89:11
MeO	$Rh_2(4S\text{-MACIM})_4$ (**35a**)	88	97:3
MeO	$Rh_2(4S\text{-MPPIM})_4$ (**35b**)	97	96:4
BnO	$Rh_2(OAc)_4$	41	49:35[a]
BnO	$Rh_2(cap)_4$	27	33:23[a]
BnO	Cu(OTf)	—	—
BnO	$Rh_2(5S\text{-MEPY})_4$ (**31a**)	81	90:9
BnO	$Rh_2(5R\text{-MEPY})_4$ (**32a**)	87	55:36[a]
BnO	$Rh_2(4S\text{-MEOX})_4$ (**33a**)	90	89:11
BnO	$Rh_2(4S\text{-MACIM})_4$ (**35a**)	94	97:3
BnO	$Rh_2(4S\text{-MPPIM})_4$ (**35b**)	93	96:4

[a] Deviation from a 100% mass balance is due to formation of the product from C–H insertion at the benzyl carbon.

The *N*-phthaloyl-amino-acid-ligated dirhodium catalysts (**40** and **41**) are the most commonly used chiral catalysts in reactions of diazoacetoacetamides.[249,250] These kinetically active carboxylate-based complexes are required for the efficient dinitrogen extrusion and generation of metallo-carbenes from diazoacetoacetamides, which have the diazo functionality highly stabilized by two adjacent electron-withdrawing groups. Due to their significantly lower reactivity towards dinitrogen extrusion, all dirhodium carboxamidates with the exception of those with azetidinone ligands (**37**) are ineffective with this class of diazo compounds. However, few cyclizations of diazoacetoacetamides using *N*-phthaloyl-amino-acid-ligated dirhodium catalysts have been reported to proceed with high enantioselectivities. The site selectivity of C–H insertion leading to the formation of

β- or γ-lactams is substrate dependent, so either lactam may be formed. Selectivity is often achieved by using substrates in which the β- or γ-position is biased toward insertion as a result of electronic or conformational effects.

As with diazoacetamides, a typical choice of amide nitrogen protecting group for diazoacetoacetamides and diazomalonamides is the *tert*-butyl group, as its methyl C–H bonds rarely undergo carbene insertion. The cyclization of acetoacetamide **125** produces β-lactam **126** with a high degree of site selectivity, although enantioselectivities are modest (Eq. 50).[64,249] The *N*-BTMSM group has also been used and gives the γ-lactam product, but enantioselectivities are modest to low.[284] Aryl rings have also been employed as nitrogen protecting groups.[250,273] Those with the *N*-4-nitrophenyl protecting group allow formation of γ-lactam products in good yields and with high diastereoselectivity.[285] As an *N*-protecting group, the electron-deficient *N*-4-nitrophenyl does not react with the metal carbene to an appreciable degree and may be removed by a two-step protocol consisting of reduction to the corresponding aniline and oxidative hydrolysis. Electron-rich aryl groups are unsuitable protecting groups because they undergo aromatic cycloaddition.[273] Enantioselectivities are highly variable; insertion into benzylic C–H bonds leads to higher enantioselectivity than insertion into alkyl C–H bonds, as shown in Eq. 50.

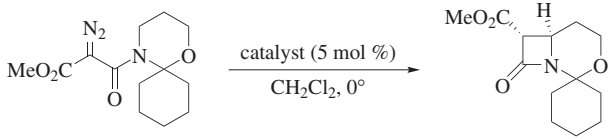


125 **126**

R	Yield (%)	% ee
Ph	94	74
n-Pr	97	60

(Eq. 50)

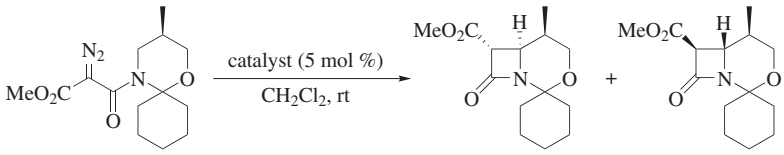
The highest levels of enantioselectivity in the C–H insertion reaction of diazoacetoacetamides occur with the reaction of *N*,*O*-acetals (e.g. Eq. 51).[286] Several catalysts with *N*-phthaloyl- and *N*-phenyl-fused phthaloyl-(*S*)-amino acids as bridging ligands provide the β-lactam **128** from substrate **127** in 83–96% ee.[286,287] With diazoacetoacetamide **129**, which has a methyl group positioned at the 5-position of a tetrahydro-1,3-oxazine ring, match/mismatch effects are seen with the $Rh_2(PTPA)_4$ (e.g., **40b**) catalysts,[288] whereas a natural selectivity toward the *syn* product **131** over the *anti* isomer **130** is seen in the absence of a chiral catalyst (Eq. 52).



127 **128**

Catalyst	Yield (%)	% ee
Rh_2(*S*-PTA)$_4$ (**40a**)	94	96
Rh_2(*S*-PTPA)$_4$ (**40b**)	89	90
Rh_2(*S*-PTV)$_4$ (**40c**)	86	92
Rh_2(*S*-PTTL)$_4$ (**40d**)	85	93

(Eq. 51)



129 **130** **131**

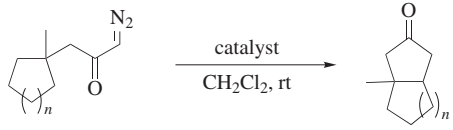
Catalyst	**130** + **131** Yield (%)	**130/131**
$Rh_2(OAc)_4$	75	25:75
Rh_2(*S*-PTPA)$_4$ (**40b**)	77	2:98
Rh_2(*R*-PTPA)$_4$ (*ent*-**40b**)	47	85:15

(Eq. 52)

Synthesis of Cycloalkane Derivatives by C–H Insertion

In contrast to C–H insertion reactions using diazoacetates and diazoacetamides and their derivatives, only a few studies report asymmetric induction in reactions of diazoketones. This paucity is due in part to the relative difficulty of their synthesis.[71] However, the principal reason is the low selectivity achieved in catalytic applications, except in special cases. The reactivity of diazoketones and diazoalkanoates toward dinitrogen extrusion are at least as good as those of diazoacetates,[32] but catalysts that are effective for high stereocontrol with diazoacetates generally do not provide high stereocontrol in reactions with diazoketones and diazoalkanoates. This dichotomy was observed early and extensively in attempts to achieve enantio-controlled intramolecular cyclopropanation reactions.[67,289,290] The cause of this considerable change in stereocontrol has been explained by conformational differences in the alignment of the keto carbene on the catalyst face.[291]

Cyclopentanones. Indicative of the challenges associated with C–H insertion reactions with diazoketones, 3-cycloalkyl-1-diazo-2-propanones **132** undergo C–H insertion catalyzed by dirhodium(II) complexes at room temperature producing the corresponding bicyclic compounds. Although good yields and diastereoselectivities are observed, very low or negligible enantioselectivities are obtained with chiral dirhodium carboxamidates (Eq. 53).[155] Low enantioselectivity is also evident in reactions catalyzed by chiral dirhodium carboxylates.[292] Hydride abstraction and subsequent ring closure is reported as a side reaction.[293]

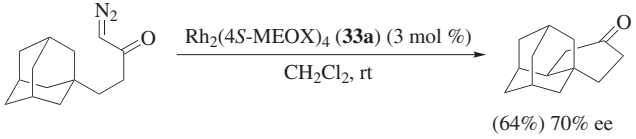


132

n	Catalyst	Yield (%)	% ee	*cis*/*trans*
2	$Rh_2(OAc)_4$	77	—	92:8
2	Rh_2(5*S*-MEPY)$_4$ (**31a**)	33	0	98:2
1	$Rh_2(OAc)_4$	80	—	100:0
1	Rh_2(5*S*-MEPY)$_4$ (**31a**)	58	0	100:0
1	Rh_2(4*S*-BNOX)$_4$ (**33c**)	78	0	100:0
1	Rh_2(4*S*-PHOX)$_4$ (**33b**)	58	7	100:0

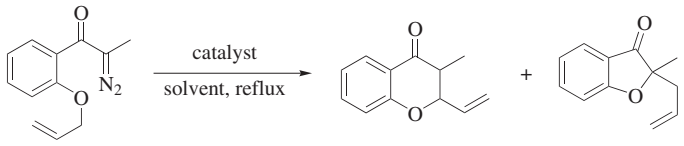
(Eq. 53)

Formation of cyclopentanones by intramolecular C–H insertion using chiral dirhodium carboxamidates is thus far poorly stereoselective, but formation of cyclohexanones can be rather enantioselective (Eq. 54).[183] In this example, only the $Rh_2(4S\text{-MEOX})_4$ (**33a**) catalyst is effective; the bicyclic cyclohexanone product is not formed when $Rh_2(MEPY)_4$, $Rh_2(MPPIM)_4$, or $Rh_2(MEAZ)_4$ is used.



(Eq. 54)

One of the first demonstrations of enantioselectivity in intramolecular C–H insertion reactions of diazoketones was with diazoketone **133** (Eq. 55).[180,294] The β-hydride elimination reaction to give an α,β-unsaturated ketone (a common competing reaction)[32] is not reported in this case, and yields are quantitative. Competition between C–H insertion yielding product **134** with ylide generation and [2,3]-sigmatropic rearrangement yielding product **135** is common and catalyst dependent.[295–297] Many other examples of highly chemoselective catalytic C–H insertion reactions of diazoketones that have moderate to low enantioselectivities have been reported,[148,298–304] and they often illustrate the unpredictability of these transformations.[148,298]



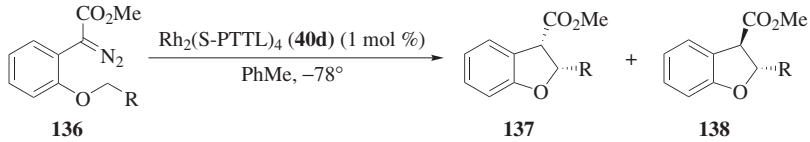
(Eq. 55)

133 **134** **135**

Catalyst	**134** Yield (%)	**135** Yield (%)	*cis*-**134**/*trans*-**134**	% ee *cis*-**134**	% ee *trans*-**134**
$Rh_2(OAc)_4$	93	7	74:26	—	0
$Rh_2(S\text{-BSP})_4$ (**39a**)	93	7	93:7	60	—
(**39d**)	96	4	85:15	31	18
(**43**)	96	4	83:17	10	7
(**44**)	82	18	75:25	20	—
(**45**)	97	3	92:8	40	—
(**46**)	90	10	92:8	8	—
$Rh_2(S\text{-mandelate})_4$ (**47**)	88	12	80:20	20	11
$Rh_2(5S\text{-MEPY})_4$ (**31a**)	96	4	74:26	0	0

2-Alkoxy-substituted methyl phenyldiazoacetates such as substrate **136** undergo highly enantioselective C–H insertion (Eq. 56).[218,305–307] Diastereoselectivity is highest with chiral phthalimido dirhodium catalysts, and with catalyst $Rh_2(S\text{-PTAD})$ (**40e**) C–H insertion is a key step in the synthesis of the natural product (–)-ephedradine.[305] Reactions performed at −78° with $Rh_2(S\text{-PTTL})_4$ (**40d**) occur with exceptionally high enantio- as well as diastereoselectivity, as

supported by the data for products **137** and **138**.[218]

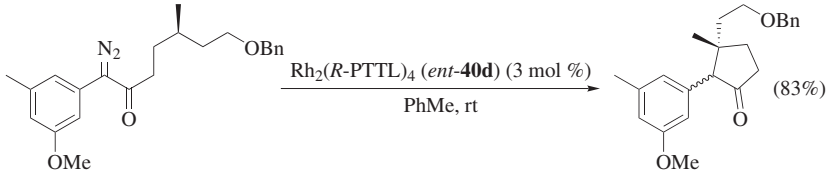


136 **137** **138**

R	**137** + **138** Yield (%)	**137**/**138**	% ee **137**	% ee **138**
Ph	86	>99:1	94	—
4-ClC_6H_4	79	>99:1	94	—
4-MeC_6H_4	84	>99:1	91	—
4-$MeOC_6H_4$	89	>99:1	94	—
3,4-$(TBSO)_2C_6H_3$	85	99:1	91	—
H_2C=CH	62	77:23	86	92
c-C_6H_{11}	63	96:4	96	—
Me	91	14:86	78	97

(Eq. 56)

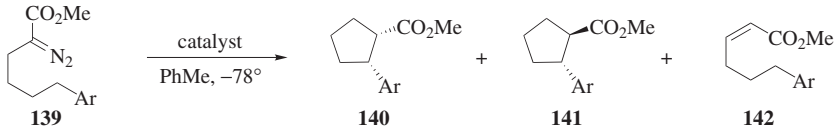
The C–H insertion reaction of diazoketones in which the diazo carbon lies between a carbonyl group and an aromatic ring illustrates the versatility of this method (Eq. 57).[308] However, although this example illustrates the effects of match/mismatch between catalyst configuration and diastereoselectivity, the diastereomeric ratio is not reported and experiments using catalyst Rh_2(*S*-PTTL)$_4$ (**40d**) are not described.



(Eq. 57)

Cyclopentanes. A suitably functionalized diazoester can give rise to cyclopentane derivatives. Very promising results are obtained using chiral dirhodium(II) phthaloyl-amino acid catalysts, as represented by the cyclization of aryl-substituted substrate **139** yielding products **140**–**142** (Eq. 58).[309] These examples demonstrate not only high enantio- and diastereoselectivities, but also the suppression of a 1,2-hydrogen shift as a side reaction.[32] An early report of intramolecular C–H insertion of a phenyldiazoacetate into a methylene group activated by adjacent nitrogen suggests that chiral copper-bisoxazolidine catalysts are more advantageous than Rh_2(5*S*-MEPY)$_4$ (**31a**) or Rh_2(*S*-TBSP)$_4$ (**39b**); but even with the former catalysts both diastereoselectivities and enantioselectivities are low,[310,311] and an alternative process for introducing enantioselectivity was eventually employed.[312] The catalyst Rh_2(*S*-PTTL)$_4$ (**40d**) affords high enantio- and diastereoselectivity in intramolecular C–H insertion reactions of

phenyldiazoacetates.[218]



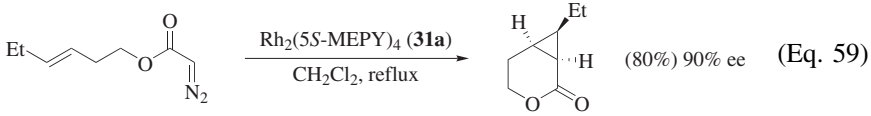
139 **140** **141** **142**

Ar	Catalyst	**140–142** Yield (%)	**140/141/142**	% ee **140**	% ee **141**
Ph	Rh_2(*S*-PTTL)$_4$ (**40d**)	85	>99:0:0	95	—
Ph	Rh_2(*S*-PTPA)$_4$ (**40b**)	66	56:37:7	89	27
Ph	Rh_2(*S*-PTA)$_4$ (**40a**)	69	73:19:8	90	56
Ph	Rh_2(*S*-PTV)$_4$ (**40c**)	68	77:20:3	95	22
4-$MeOC_6H_4$	Rh_2(*S*-PTTL)$_4$ (**40d**)	85	>99:0:0	92	—
4-ClC_6H_4	Rh_2(*S*-PTTL)$_4$ (**40d**)	81	>99:0:0	93	—

(Eq. 58)

Side Reactions

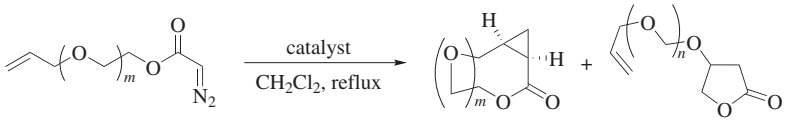
The competition between intramolecular cyclopropanation and C−H insertion provides an instructive illustration of the effects of catalyst selection on chemoselectivity toward the C−H insertion processes in unsaturated substrates.[313] Allylic and homoallylic diazoacetates (Eq. 59) undergo intramolecular cyclopropanation in preference to C−H insertion,[314] and the enantioselectivities vary dramatically with the chiral catalyst employed.[313] In general, rhodium-carboxamidate-ligated complexes favor C−H insertion, whereas copper- and rhodium-carboxylate complexes favor cyclopropanation.



(Eq. 59)

This trend also holds for diazo compounds having longer chains. With dirhodium carboxamidate catalysts substrates **143** undergo nearly exclusive C−H insertion to form γ-butyrolactones **145** with high enantioselectivity, whereas products of intramolecular cyclopropanation **144** are formed preferentially but with low enantioselectivity when more reactive dirhodium carboxylates and Cu(box)PF_6 are employed (Eq. 60).[313] That the competition between cyclopropanation and C−H insertion is related to the electronic ligand-controlled bias placed on the metal was first suggested by results from dirhodium catalysts having achiral ligands.[137,142,316] Results obtained with Rh_2(4*S*-IBAZ)$_4$ (**37b**), which is electronically more reactive than the other dirhodium carboxamidates, support this interpretation. Preferential C−H insertion to form γ-butyrolactone products with high enantioselectivity is generally reported for chiral dirhodium carboxamidate-catalyzed reactions of diazo compounds that have remote, potentially reactive, functional groups.[315,317–319] The only exceptions are found

when access to a γ-CH group is sterically prevented.[320,321]



143 **144** **145**

144 + **145** (50–95%)

m	*n*	Catalyst	**144/145**	% ee **144**
1	0	Rh_2(5*S*-MEPY)$_4$ (**31a**)	<1:99	—
1	0	Rh_2(4*S*-MEOX)$_4$ (**33a**)	<1:99	—
1	0	Rh_2(4*S*-MPPIM)$_4$ (**35b**)	—	—
1	0	Rh_2(4*S*-IBAZ)$_4$ (**37b**)	5:95	49
1	0	Rh_2(*S*-TBSP)$_4$ (**39b**)	95:5	28
1	0	Cu(box)PF_4	—	71
2	1	Rh_2(5*S*-MEPY)$_4$ (**31a**)	5:95	53
2	1	Rh_2(4*S*-MEOX)$_4$ (**33a**)	1:99	48
2	1	Rh_2(4*S*-MPPIM)$_4$ (**35b**)	—	—
2	1	Rh_2(4*S*-IBAZ)$_4$ (**37b**)	42:58	56
2	1	Rh_2(*S*-TBSP)$_4$ (**39b**)	98:2	11
2	1	Cu(box)PF_4	100:0	79

(Eq. 60)

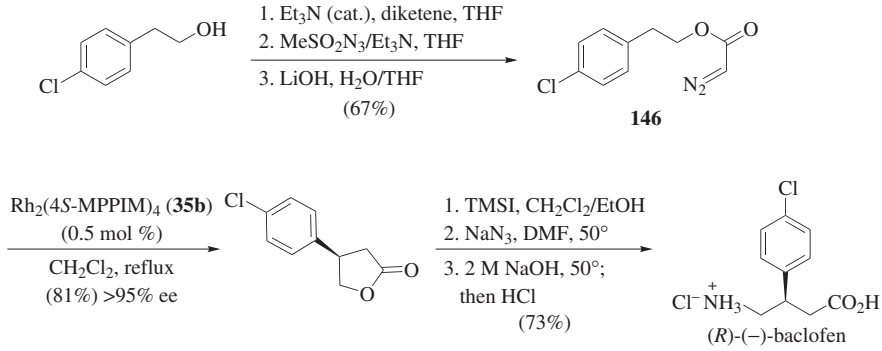
To minimize competing "carbene dimerization," reactions of diazoacetates are commonly performed by slow, controlled addition of the diazoacetate to the catalyst solution.[322–325] This competing reaction arises from electrophilic addition of the metal carbene to excess diazoacetate. Thus, limiting the concentration of the diazo compound decreases the rate of formation of the carbene dimer.[322] Maleate and fumarate "carbene dimer" products ($RO_2C–CH=CH–CO_2R$) can themselves undergo dipolar cycloaddition with the reactant diazoacetate, but these products are rarely identified. The formation of azines ($RO_2C–CH=N–N=CH–CO_2R$) in these reactions remains poorly understood, but the reaction pathway is not believed to be associated with the catalyst. These basic compounds coordinate with the catalyst and inhibit the reaction.[322]

As exemplified in Eq. 58 (product **142**), the 1,2-hydrogen shift is competitive with other metal carbene transformations of diazoalkanoates and similar diazoketones.[32,326,327] This reaction is often significant except when hydrogen migration from a methyl group is involved. The catalyst influences the extent of this competing reaction, but its complete suppression has rarely been reported.[309,326]

APPLICATIONS TO SYNTHESIS

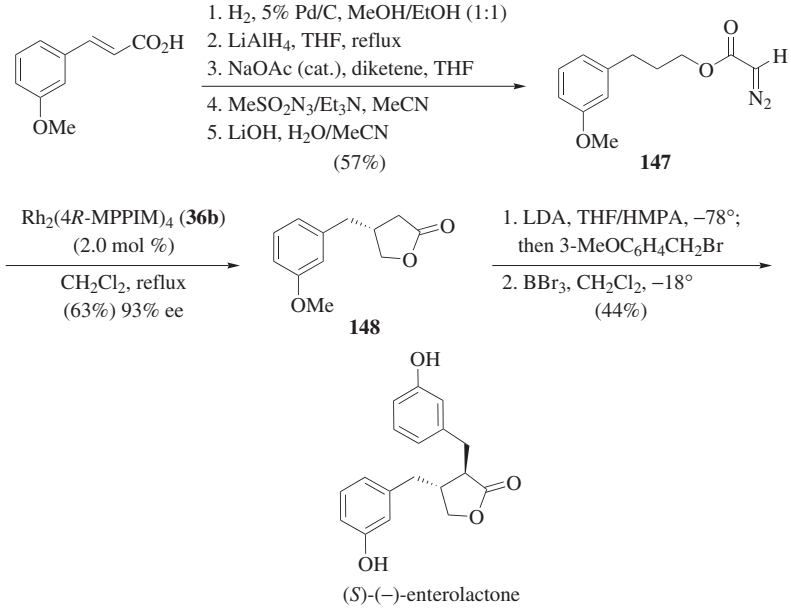
Examples of biologically active compounds that have been prepared in greater than 90% ee by intramolecular C–H insertion include lignan lactones (see Scheme 9 in "Comparison with Other Methods")[259,260] and the 2-deoxyxylolactone **25** (Eq. 12).[153,154] The reaction of 2-(4-chlorophenyl)ethyl diazoacetate (**146**) with only 0.5 mol % Rh_2(4*S*-MPPIM)$_4$ (**35b**) results in insertion into the benzylic C–H

bond in 81% yield and 95% ee (Scheme 5). This reaction was applied to the synthesis of (*R*)-(−)-baclofen, a therapeutically effective GABA receptor agonist.[328] The related 2-phenyl-1-ethyl diazoacetate gives the corresponding lactone in 42% yield and 46% ee with $Rh_2(5S\text{-MEPY})_4$ (**31a**) as catalyst.[258] The $Rh_2(MPPIM)_4$ catalysts are thus optimal for high enantiocontrol in the intramolecular C−H insertion reactions of alkyl diazoacetates.



Scheme 5

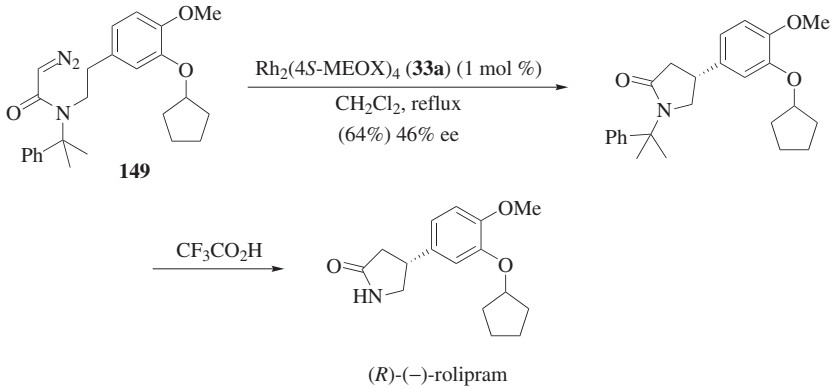
The construction of the natural lignan lactone (*S*)-(−)-enterolactone[223,259] is also illustrative of the synthetic advantages of this method (Scheme 6). C−H



Scheme 6

insertion on diazoacetate **147** with catalyst $Rh_2(4R\text{-MPPIM})_4$ (**36b**) results in the formation of β-substituted γ-lactone **148** with the absolute configuration at C-4 established as (*R*). Subsequent alkylation and demethylation forms (*S*)-(−)-enterolactone. Use of $Rh_2(4S\text{-MPPIM})_4$ (**35b**) forms the product of opposite chirality and provides access to (*R*)-(−)-enterolactone. The predictability of absolute configuration with these catalysts has allowed configurational assignment in the synthesis of imperanene.[260]

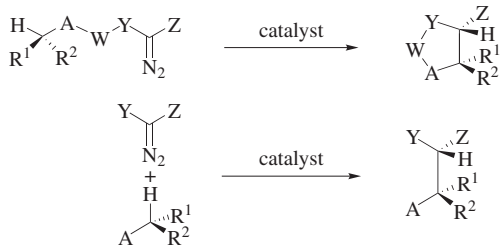
(*R*)-(−)-Rolipram, a selective inhibitor of phosphodiesterase type IV, is prepared in 46% ee by C–H insertion with diazoacetamide **149**, followed by standard transformations (Scheme 7).[275]



Scheme 7

COMPARISON WITH OTHER METHODS

Catalytic, asymmetric, intramolecular C–H insertion provides convenient access to 5- and 4-membered ring lactones, lactams, and, in selective instances, cyclopentanes with moderate to high selectivities. The method is direct, insertion is stereospecific at the C–H bond undergoing insertion, and stereoselectivity can be controlled. Catalyst loading can be lowered to <1.0 mol %, and catalysts could, in principle, be recovered.[32] Although the target compounds can often be prepared by more conventional methods,[329] the catalytic metal carbene approach effects C–H functionalization and stereocontrol in the same reaction process, thereby providing superior efficiency in the number of steps required for the synthesis. Directly comparable alternative methods that incorporate C–H insertion with the construction of a C–C bond are not available, and therefore the following discussion will focus on the advantages and disadvantages of intramolecular versus intermolecular C–H insertion (Scheme 8).



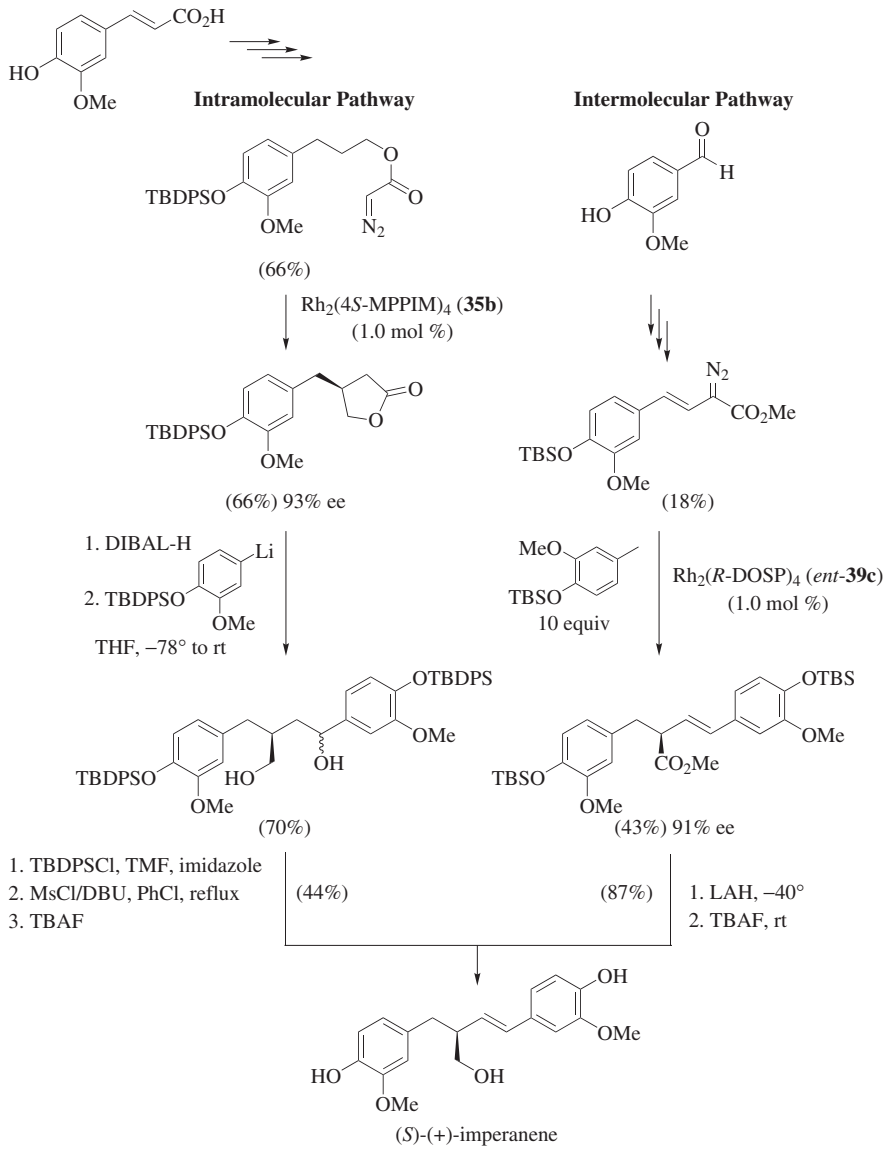
Scheme 8

Intramolecular catalytic C–H insertion was utilized as a synthetic method before intermolecular applications because of the greater ability to control site selectivity with intramolecular reactions.[39,59] Achievement of high stereo- and site selectivity in intermolecular C–H insertion has been a significant advance in C–H functionalization.[59] The broad spectrum of substrates for C–H insertion offers unlimited possibilities. However, thus far these reactions are achievable only with donor–acceptor metallo-carbene species such as those derived from aryldiazoacetates or styryldiazoacetates.[7,19] A direct comparison between inter- and intramolecular C–H insertion approaches to a specific natural product has been made.[59] The yield-related advantages of the intramolecular approach are evident in an (*S*)-(+)-imperanene synthesis (Scheme 9). On the other hand, the fewer steps and the convenience of the chemistry in the intermolecular version represent a distinctive advantage, at least in this case. Few other direct comparisons exist, and the applications of inter- and intramolecular C–H insertion reactions applied to organic synthesis remain distinct.

EXPERIMENTAL CONDITIONS

The handling of diazocarbonyl compounds should follow the normal precautions used for compounds that are potentially toxic and subject to explosive decomposition. However, because the carbonyl group imparts stability to the adjacent diazo functionality, diazocarbonyl compounds have a much higher thermal stability than do diazomethane and other diazoalkanes. For example, the half life for decomposition of ethyl diazoacetate at 100° in mesitylene is 109 hours, and that for the decomposition of 1-diazo-2-cyclohexanone is 32 minutes, compared to 3 hours for the decomposition of 2-diazopropane at 0° in diethyl ether.[32] In fact, ethyl diazoacetate can be purified by distillation at atmospheric pressure (b.p. 140–141°). For those diazocarbonyl compounds that are formed by diazo transfer from sulfonyl azides, care must be taken in the handling of the azide reagent. Studies of their thermal stability, ease of handling, and safety have been reported,[201,202] and from examination of twelve sulfonyl azides the commonly used methanesulfonyl azide was determined to pose the greatest hazard.

Diazocarbonyl compounds are unstable toward strong Brønsted and Lewis acids, but ethyl diazoacetate and similarly stable diazo esters survive treatment with glacial acetic acid at room temperature. They can also be decomposed



Scheme 9

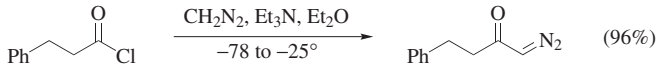
by prolonged exposure to light and, as is the subject of this review, treatment with select transition-metal complexes. Catalyzed reactions are commonly performed under simulated high-dilution conditions, especially with diazoacetates, diazoacetamides, and diazoketones having the structure $RC(O)CHN_2$, to minimize "carbene dimerization" that is often the major competing reaction. Dropwise

addition of the dilute diazocarbonyl compound or controlled addition by syringe pump is the commonly used experimental condition.

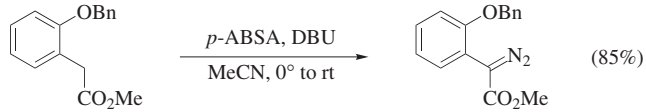
The presence of Lewis bases in the reaction medium, even those that are functional groups on the substrate, can interfere with the desired reaction by either occupying the catalytically active center of the transition metal or by reacting with the intermediate metallo-carbene. Water commonly interferes through catalytic reactions with the diazocarbonyl compound to form the corresponding α-hydroxy compound. The solvents employed for diazo decomposition reactions are hydrocarbons, dichloromethane, 1,2-dichloroethane, or toluene. Benzene, a carcinogen, has been used in some investigations, but it does not offer special advantages that could not be reproduced with an alternative solvent such as toluene.

EXPERIMENTAL PROCEDURES

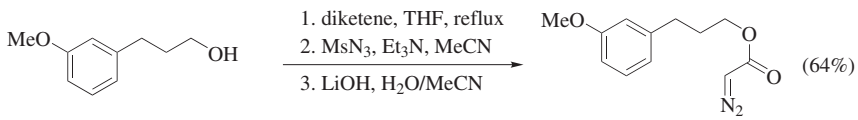
Preparation of Diazo Compounds



1-Diazo-4-phenylbutan-2-one [Arndt–Eistert Reaction].[170] Dry NEt_3 (11.1 mL, 80 mmol) was added to 350 mL of an anhydrous ethereal solution of diazomethane (80 mmol, 200 mL of 0.4 M solution) under N_2 in a dry 1-L Morton flask fitted with a mechanical stirrer, a dropping funnel, and a low-temperature thermometer. The solution was cooled to -78° (dry ice/acetone) and 11.8 mL of 3-phenylpropanoyl chloride (80 mmol) in 40 mL of anhydrous Et_2O was added dropwise with vigorous stirring over 25 min. A thick slurry formed during the addition. The reaction mixture was stirred an additional 15 min at -78° and then for 1 h at -25° to -20° (dry ice/H_2O/$CaCl_2$). During the course of the reaction, the mixture became more viscous and then thinned out again. After warming to rt, the reaction mixture was diluted with water. The organic layer was separated and washed successively with 10% aqueous acetic acid, water, sat. $NaHCO_3$ solution, and brine. The resulting solution was dried over $CaSO_4$ and concentrated under vacuum to give the title compound as a deep yellow oil (12.8–13.5 g, 76–80 mmol, 92–100%), having spectral properties identical to those reported:[330] IR (neat) 3087 (m), 2928 (w), 2105 (s), 1638 (s), 1454 (w), 1376 (s), 1140 (m), 1099 (m), 751 (m), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 2H), 7.26–7.15 (m, 3H), 5.21 (br s, 1H), 2.98 (t, $J = 7.7$ Hz, 2H), 2.66 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9 (C), 140.7 (C), 128.6 (2 x CH), 128.4 (2 x CH), 126.3 (CH), 54.6 (CH), 42.4 (CH_2), 31.0 (CH_2); UPLC/MS: $t_R = 2.28$ min (100%, $m/z + 1 = 175$); HRMS–ES$^+$ (m/z): $[M + H]^+$ calcd for $C_{10}H_{10}N_2O$, 175.08659; found, 175.08670.



Methyl 2-(2-(Benzyloxy)phenyl)-2-diazoacetate [Diazo Transfer Reaction].[218] To a solution of methyl 2-(2-benzyloxy)phenylacetate (2.0 g, 7.8 mmol) and 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 5.6 g, 23.4 mmol) in MeCN (10 mL) at 0° was added dropwise 1,8-diazabicylo-7-undecene (4.7 mL, 31.2 mmol). The mixture was stirred at rt for 24 h. The resulting orange mixture was partitioned between EtOAc (100 mL) and water (50 mL). The organic layer was washed successively with 10% aq NaOH, water, and brine, and dried over Na_2SO_4. Filtration and evaporation afforded 2.1 g of crude product as an orange oil. The latter was purified by column chromatography on silica gel (hexane/EtOAc = 8 : 1) to provide the title compound (1.9 g, 6.7 mmol, 85%) as an orange oil: IR (film) 2099, 1701, 1254 cm^{-1}; ^1H NMR (270 MHz, C_6D_6) δ 7.82 (m, 1H), 7.17–6.85 (m, 7H), 6.54 (m, 1H), 4.56 (s, 2H), 3.34 (s, 3H); ^{13}C NMR (67.8 MHz, C_6D_6) δ 165.9, 154.9, 136.7, 130.7, 128.7, 128.4, 128.2, 127.6, 121.6, 114.6, 112.4, 70.7, 59.8, 51.4; HRMS–EI (m/z): M^+ calcd for $C_{16}H_{14}N_2O_3$, 282.1004; found, 282.1028. Anal. Calcd for $C_{16}H_{14}N_2O_3$: C, 61.95; H, 7.80; N, 5.16. Found: C, 61.84; H, 7.72; N, 5.08.

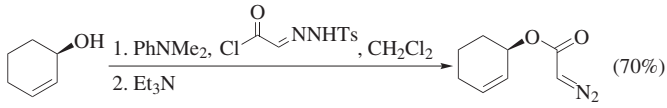


3-(3-Methoxyphenyl)propyl 2-Diazoacetate [Acyl Cleavage Reaction].[223] To a solution of 3-(3-methoxyphenyl)propan-1-ol (6.2 g, 37 mmol) in anhydrous THF (50 mL) was added NaOAc (80 mg, 1.0 mmol), and then a solution of diketene (4.8 g, 55 mmol, 1.5 equiv) in THF (10 mL) was added dropwise at rt. The resulting solution was continually stirred for 10 h at rt, then was heated to reflux for 1.5 h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 3 : 1 to 2 : 1) to provide a colorless oil (8.8 g, 35 mmol, 95%) identified as 3-(3-methoxyphenyl)propyl acetoacetate: ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (td, J = 7.4, 1.2 Hz, 1H), 6.77 (d, J = 7.4 Hz, 2H), 2.28 (s, 3H), 2.03–1.93 (m, 2H) with the enol form at 5.02 (s, 1H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 159.7, 142.6, 129.5, 120.8, 114.2, 111.3, 64.7, 55.2, 50.1, 32.1, 30.2, 30.0.

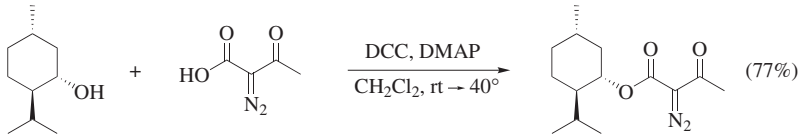
A solution of methanesulfonyl azide (6.6 g, 54 mmol, 1.5 equiv) in anhydrous acetonitrile (70 mL) was added dropwise over 20 min to a solution of 3-(3-methoxyphenyl)propyl acetoacetate (8.8 g, 35 mmol) and NEt_3 (5.5 g, 54 mmol, 1.5 equiv) in anhydrous acetonitrile (60 mL). The resulting yellow solution was stirred for 12 h at rt, after which the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 2 : 1 to 1 : 1) to give 3-(3-methoxyphenyl)propyl diazoacetoacetate

(10.3 g, 32 mmol, 90% yield, ~85% pure): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (t, $J = 7.8$ Hz, 1H), 6.76–6.68 (m, 3H), 4.24 (t, $J = 6.5$ Hz, 2H), 3.77 (s, 3H), 2.68–2.63 (m, 2H), 2.44 (s, 3H), 2.05–1.95 (m, 2H).

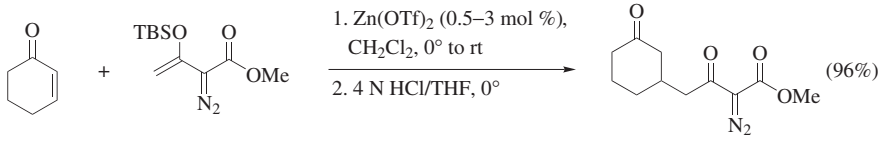
The diazoacetoacetate (10.3 g, 32 mmol) was dissolved in 40 mL of MeCN and added in one portion to a solution of $LiOH{\bullet}H_2O$ (4.9 g, 117 mmol, 3.7 equiv) in H_2O (100 mL). The reaction mixture was stirred for 1.5 h at rt whereupon the resulting dark-brown solution was extracted with EtOAc (3 × 75 mL), and the organic extract was then washed with brine (75 mL), sat. aq citric acid (75 mL), and brine (2 × 75 mL). After drying over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 3 : 1) to afford the title compound (5.50 g, 23.5 mmol, 74%) as a yellow oil: IR (film) 2113, 1695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (dd, $J = 8.7$, 7.6 Hz, 1H), 6.77–6.70 (m, 3H), 4.74 (br s, 1H), 4.16 (t, $J = 6.6$ Hz, 2H), 3.77 (s, 3H), 2.65 (t, $J = 7.8$ Hz, 2H), 1.95 (tt, $J = 7.8$, 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 142.5, 129.2, 120.6, 114.0, 111.1, 63.9, 54.9, 45.9, 31.9, 30.1. Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.02; N, 11.96. Found: C, 61.46; H, 5.99; N, 12.02.



(*R*)-Cyclohex-2-en-1-yl 2-Diazoacetate [Direct Diazoacetylation].[224] Dry *N*,*N*-dimethylaniline (1.55 g, 12.24 mmol) was added to a cold (0°) and stirred solution of *R*-2-cyclohexen-1-ol (1.0 g, 10.2 mmol) and [(4-toluenesulfonyl) hydrazono]acetyl chloride (3.31 g, 12.75 mmol) in dry CH_2Cl_2 (68 mL). After 20 min at 0°, dry NEt_3 (7.1 mL, 51 mmol) was injected over about 1 min and stirring was continued for 15 min. The cold bath was removed, and, after a further 30 min, the mixture was quenched with water (30 mL) and concentrated. The residue was extracted with EtOAc/hexane (1 : 9, 2 × 65 mL), and the combined extracts were washed with sat. aq citric acid (2 × 30 mL). The combined aqueous layers were extracted with EtOAc/hexane (1 : 9, 30 mL), and the organic extract was washed with sat. aq citric acid (5 mL). All the organic extracts were combined, dried over $MgSO_4$ and evaporated. Flash column chromatography of the residue over silica gel (4 × 20 cm, EtOAc/hexane = 1 : 12) afforded the title compound (1.19 g, 7.2 mmol, 70%) as a bright yellow oil containing trace impurities. The material was distilled (Kugelrohr, 45°, 0.05 mm Hg) for characterization: FT–IR ($CHCl_3$ cast) 3120, 2950, 2055, 1690, 1380, 1180 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (ddt, $J = 10.0$, 3.8, 1.2 Hz, 1H), 5.72 (ddt, $J = 10.0$, 3.8, 2.1 Hz, 1H), 5.35 (m, 1H), 4.74 (br s, 1H), 2.18–1.81 (m, 3H), 1.81–1.55 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 132.7, 125.7, 68.6, 28.5, 24.9, 18.6; HRMS (m/z): M^+ calcd for $C_8H_{10}N_2O_2$, 166.0742; found, 166.0725. Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.06; N, 16.86. Found: C, 57.81; H, 5.98; N, 16.81.



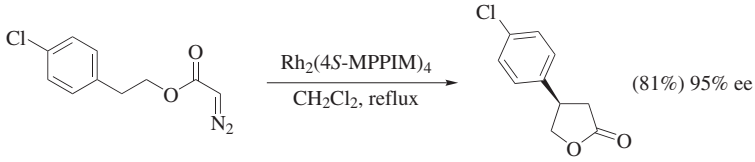
D-(+)-Menthyl Diazoacetoacetate [DCC Coupling Reaction].[77] To a solution of D-(+)-menthol (78 mg, 0.50 mmol), diazoacetoacetic acid (154 mg, 1.2 mmol) and DMAP (6 mg, 0.05 mmol) in CH_2Cl_2 (3.3 mL) at rt was added in one portion DCC (206 mg, 1.0 mmol). The reaction mixture was heated at 40° until the reaction was complete (60–90 min). The mixture was filtered through a plug of Celite (Et_2O as eluent), and the resulting filtrate was partitioned between H_2O and Et_2O. The aqueous layer was extracted twice with Et_2O. The organic extracts were combined, washed with sat. aq $NaHCO_3$ and then with brine. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by column chromatography (hexane/EtOAc = 9 : 1) giving the title product (87 mg, 0.39 mmol, 77%) having spectral properties identical to those previously reported:[121] $[\alpha]_D^{25}$ −88.7 (c = 2.15, $CHCl_3$); IR (thin film) 2139, 1712, 1662 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.82 (dt, J = 10.9, 4.4 Hz, 1H), 2.48 (s, 3H), 2.10–2.02 (m, 1H), 1.84 (d quin, J = 7.0, 2.7 Hz, 1H), 1.76–1.65 (m, 2H), 1.60–1.32 (m, 3H), 1.18–0.98 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H), 0.80 (d, J = 6.9 Hz, 3H). Anal. Calcd for $C_{14}H_{22}N_2O_3$: C, 63.18; H, 8.33; N, 10.52. Found: C, 63.26; H, 8.38; N, 10.61.



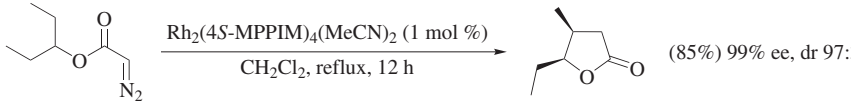
Methyl 2-Diazo-3-oxo-4-(3-oxocyclohexyl)butanoate [Mukaiyama–Michael Reaction].[75] To a flame-dried, 25-mL, round-bottomed flask under nitrogen was added zinc triflate (5.5 mg, 0.015 mmol), followed by 2-cyclohexen-1-one (49 mg, 0.50 mmol) and dry CH_2Cl_2 (2 mL). The mixture was stirred at 0°. Methyl 3-*tert*-butyldimethylsilanyloxy-2-diazobut-3-enoate (202 mg, 0.750 mmol) was added via syringe all at once. The yellow solution was stirred at 0° for 1 h and then was allowed to warm slowly to rt. After 16 h the crude reaction mixture was concentrated under reduced pressure. The residue was dissolved in THF (5 mL) and stirred at 0°, then an aq HCl (4 M, 1.0 mL) solution was added dropwise. After 1 h at 0° the reaction was quenched by slow addition of sat. $NaHCO_3$ (15 mL) solution until basic to pH paper. The resulting solution was extracted with three 10-mL portions of CH_2Cl_2, and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with EtOAc/hexane (1 : 2) to give the title compound (114 mg, 0.48 mmol, 96%) as a light yellow oil: IR

(neat) 2137, 1712, 1652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 2.86 (dd, $J = 15.7$, 6.5 Hz, 1H), 2.76 (dd, $J = 15.7$, 6.5 Hz, 1H), 2.37–2.13 (mp, 4H), 2.06–1.85 (mp, 3H), 1.65–1.55 (m, 1H), 1.39–1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 190.7, 161.6, 76.1, 52.2, 47.4, 46.0, 41.1, 35.0, 31.0, 24.9; HRMS–FAB (m/z): $[M + H]^+$ calcd for $C_{11}H_{14}N_2O_4$, 239.1032; found, 239.1035.

Catalytic, Asymmetric, Intramolecular C–H Insertions

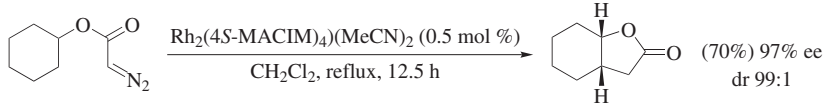


(*R*)-4-(4-Chlorophenyl)dihydrofuran-2(3*H*)-one [Synthesis of a β-Substituted γ-Butyrolactone from an Acyclic Diazoacetate].[329] A solution of 4-chlorophenethyl 2-diazoacetate (708 mg, 3.2 mmol) in dry CH_2Cl_2 (20 mL) was added, over a period of 5 h via a syringe pump, to a refluxing solution of $Rh_2(4S\text{-MPPIM})_4$ (22 mg, 0.016 mmol) in dry CH_2Cl_2 (80 mL). The solvent was evaporated under vacuum and the crude residue was purified by chromatography on silica gel (hexanes/EtOAc = 4 : 1) to afford the title compound (502 mg, 2.56 mmol, 81%) as a white solid: $[\alpha]_D^{26}$ −50.9 ($c = 0.7$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 4.65 (dd, $J = 9.0$, 7.5 Hz, 1H), 4.22 (dd, $J = 9.0$, 7.5 Hz, 1H), 3.76 (pent, $J = 9.0$ Hz, 1H), 2.92 (dd, $J = 17.5$, 9.0 Hz, 1H), 2.62 (dd, $J = 17.5$, 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 133.5, 129.2, 128.0, 75.9, 73.7, 40.3, 35.5; HRMS (m/z): $[M + H]^+$ calcd for $C_{10}H_9O_2Cl$, 197.0369; found, 197.0372. The enantioselectivity was determined as follows: a sample of the γ-butyrolactone was reduced with a THF solution of $LiAlH_4$ to give the corresponding diol, followed by treatment with excess trifluoroacetic anhydride to give the (bis)trifluoroacetate ester. The ee (95%) was determined by GC on a 30-m Chiraldex B-DM column: $t_R(R) = 99.6$ min, $(S) = 100.4$ min (flow rate: 1.0 mL/min, oven temperature 100° for 20 min, then 0.5°/min to 140°).

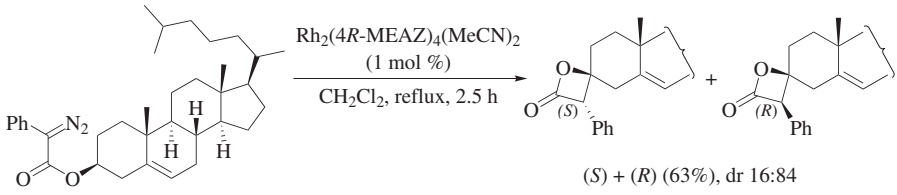


(4*S*,5*S*)-5-Ethyl-4-methyldihydrofuran-2(3*H*)-one [Desymmetrization of a Secondary Alkyl Diazoacetate].[152] To a refluxing solution of $Rh_2(4S\text{-MPPIM})_4$

$(MeCN)_2$ (14 mg, 0.010 mmol) in anhydrous CH_2Cl_2 (20 mL) was added pentan-3-yl 2-diazoacetate (156 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) over a 12 h period. The solvent was removed on a rotary evaporator. The product was purified by distillation (12 mm Hg, 105°) to yield the γ-lactone product (109 mg, 0.85 mmol, 85%) as a colorless oil in 99% ee. The enantiomeric composition was determined by CSP–GC with baseline separation on a B-PH column. The spectral properties were identical to those previously reported:[331] $[\alpha]_D^{25}$ −34.4 (c = 2.0, $CHCl_3$); IR (neat) 1777, 1466, 1223, 1128, 811 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.64–3.55 (m, 1H), 2.70 (dd, J = 16.8, 7.6 Hz, 1H), 2.60–2.40 (m, 1H), 2.2 (dd, J = 16.8, 3.0 Hz, 1H), 2.00–1.85 (m, 2H), 1.12 (d, J = 7.5 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 111.7, 37.5, 34.5, 26.6, 14.3, 13.5; EIMS (70 eV) m/z: 128, 99, 71, 59, 42.

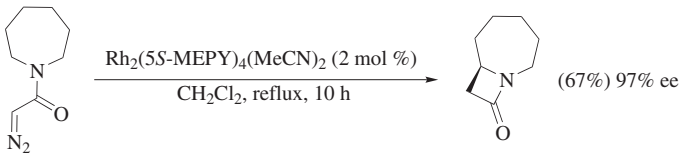


(3a*S*,7a*S*)-Hexahydrobenzofuran-2(3*H*)-one [Formation of a Bicyclic γ-Lactone from a Cyclic Diazoacetate].[243] To a light-blue solution of $Rh_2(4S\text{-}MACIM)_4(MeCN)_2$ (5.1 mg, 0.0050 mmol) in refluxing anhydrous CH_2Cl_2 (50 mL) was added a solution of cyclohexyl 2-diazoacetate (168 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) through a syringe pump at a rate of 0.8 mL/h (12.5 h). After addition was complete, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 9 : 1) to give the title compound (98 mg, 0.70 mmol, 70%) as a colorless oil in 97% ee: $[\alpha]_D^{26}$ −34.4 (c 0.41, MeOH); IR (film) 1776 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.51 (q, J = 4.1 Hz, 1H), 2.61 (dd, J = 16.8, 6.7 Hz, 1H), 2.45–2.33 (m, 1H), 2.24 (dd, J = 16.8, 2.5 Hz, 1H), 2.14–2.02 (m, 1H), 2.01–1.18 (m, 7H). Enantiomeric separations were performed on a Chiraldex G-TA column with baseline separation at 130°: t_R (1*R*,6*R*) = 50.2 min, t_R (1*S*, 6*S*) = 50.9 min.

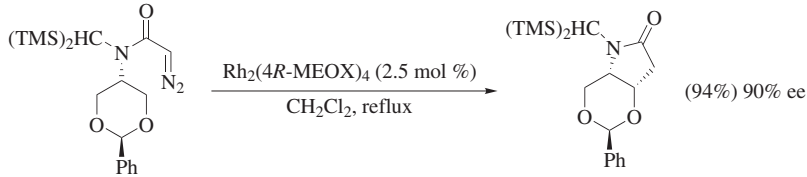


(2*S*) and (2*R*)-3-(3β-Hydroxy-5-cholesten-3α-yl)phenylacetic Acid Lactones [β-Lactone Formation from a Phenyldiazoacetate].[135] To a stirred

solution of $Rh_2(4S\text{-MEAZ})_4(MeCN)_2$ (3.8 mg, 0.0047 mmol) in dry CH_2Cl_2 (5.0 mL) heated at reflux under an argon atmosphere was added the steroidal phenyl diazoacetate substrate (250 mg, 0.47 mmol) in dry CH_2Cl_2 (3.0 mL) over 2 h via syringe pump. The reaction mixture was heated at reflux for an additional 30 min upon completion of the addition. After cooling to rt, the mixture was filtered through a short silica plug, which was subsequently washed with EtOAc/hexanes (1 : 4, 25 mL). The solvent was removed under reduced pressure to afford 239 mg of the crude product as an off-white crystalline solid. ^{1}H NMR analysis of the reaction mixture showed the presence of (2*S*)- and (2*R*)-3-(3β-hydroxy-5-cholesten-3α-yl)phenylacetic acid lactones in 69% yield. Column chromatography on silica gel (hexanes/EtOAc = 19 : 1) afforded a mixture of the isomeric (*S*) and (*R*) title products (149 mg 0.30 mmol, 63%) as white crystals, dr = 16 : 84 as determined by ^{1}H NMR (600 MHz). Analytical separation of these two products was achieved by column chromatography (silica gel, β-lactones loading ratio 100 : 1, EtOAc/hexanes = 1 : 100 to 1 : 50) to afford each as a white solid film. (2*S*)-3-(3β-Hydroxy-5-cholesten-3α-yl)phenylacetic Acid Lactone: IR ($CDCl_3$) 1816 (C=O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.30 (m, 3H), 7.16 (dd, J = 8.0, 1.7 Hz, 2H), 5.63–5.59 (m, 1H), 4.46 (s, 1H, α-H β-lactone), 3.05 (dddd, J = 13.3, 2.7, 2.6, 2.4 Hz, 1H, C4–H_{ax}), 2.15 (dd, J = 13.3, 2.8 Hz, 1H, C4–H_{eq}), 2.12–2.04 (m, 1H), 1.98 (ddd, J = 18.5, 13.9, 4.7 Hz, 1H, C2–H_{ax}), 1.96- 1.91 (m, 1H), 1.88–1.80 (m, 1H), 1.80–1.74 (m, 1H, C2–H_{eq}), 1.70–0.95 (m, 19H), 1.01 (s, 3H), 0.89 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.73 (ddd, J = 16.0, 12.2, 4.7 Hz, 1H), 0.66 (s, 3H), 0.40 (ddd, J = 18.3, 14.0, 4.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 138.7, 130.9, 129.5, 128.6, 128.2, 124.2, 83.8, 63.6, 56.6, 56.2, 50.4, 44.6, 42.3, 39.5, 36.2, 35.7, 35.2, 32.1, 31.9, 29.7, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.2, 18.7, 11.8; HRMS–FAB$^+$ (m/z): [M + H]$^+$ calcd for $C_{35}H_{50}O_2$, 503.3889; found, 503.3889. (2*R*)-3-(3β-Hydroxy-5-cholesten-3α-yl)phenylacetic Acid Lactone: IR ($CDCl_3$) 1817 (C=O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.25 (m, 3H), 7.15 (dd, J = 8.3, 1.5 Hz, 2H), 4.48 (s, 1H, α-*H* β-lactone), 4.13–4.09 (m, 1H), 2.66 (dddd, J = 13.8, 2.9, 2.8, 2.5 Hz, 1H, C4–H_{ax}), 2.30 (dddd, J = 17.1, 14.2, 3.9, 1.0 Hz, 1H, C2–H_{ax}), 2.15 (dd, J = 13.8, 2.8 Hz, 1H, C4–H_{eq}), 2.07–1.99 (m, 2H), 1.96 (dddd, J = 12.9, 3.3, 3.2, 3.1 Hz, 1H, C2–H_{eq}), 1.85–1.76 (m, 1H), 1.70–1.63 (m, 1H), 1.56–1.05 (m, 18H), 1.04–0.85 (m, 3H), 0.99 (s, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.81 (ddd, J = 16.6, 11.9, 5.2 Hz, 1H), 0.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 135.7, 130.8, 129.6, 128.1, 128.0, 124.0, 82.8, 63.8, 56.6, 56.2, 50.2, 42.3, 39.7, 39.5, 38.1, 36.4, 36.2, 36.1, 35.7, 33.8, 31.9, 31.7, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.1, 19.2, 18.7, 11.8; HRMS–FAB$^+$ (m/z): [M + H]$^+$ calcd for $C_{35}H_{50}O_2$, 503.3889; found, 503.3889.

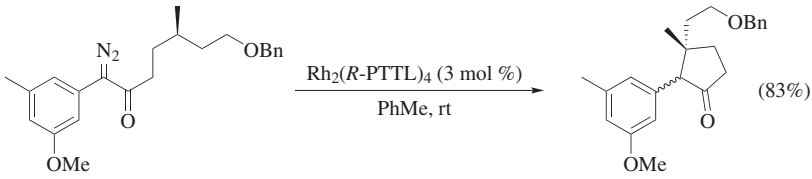


(*R*)-1-Azabicyclo[5.2.0]nonan-9-one [β-Lactam Formation from a Diazoacetamide].[277] To a solution of $Rh_2(5S\text{-MEPY})_4(MeCN)_2$ (17.2 mg, 0.020 mmol) in refluxing anhydrous CH_2Cl_2 (50 mL), 1-(azepan-1-yl)-2-diazoethanone (167 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added by syringe pump at a rate of 1.0 mL/h (10 h). After addition was complete, the reaction mixture was concentrated under reduced pressure, and the catalyst was removed by passing the chloroform solution through a silica gel plug. The solvent was removed under reduced pressure and the residue was distilled. Fractions with boiling points of 90–100° at 0.07 mm Hg were collected to yield the title β-lactam (93 mg, 0.67 mmol, 67%) as an oil in 97% ee. Enantiomer separation was achieved on a 30-m Chiraldex B-PH column at 120°: t_R (minor) = 87.2 min, t_R (major) = 88.2 min; $[\alpha]_D^{21}$ +55.0 (*c* 1.93, $CHCl_3$). The spectral properties were identical to those previously reported:[332] IR (film) 1745 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 3.61 (br s, 1H), 2.85 (dd, J = 14, 5 Hz, 1H), 2.30 (dd, J = 14, 3 Hz, 1H); MS (m/z): 139 (100).

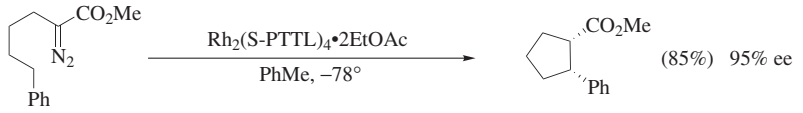


(2*S*,4a*S*,7a*S*)-5-(bis(Trimethylsilyl)methyl)-2-phenyltetrahydro-[1,3]dioxino[5,4-*b*]pyrrol-6(4*H*)-one [γ-Lactam Formation from a Diazoacetamide].[281] A solution of *N*-(bis(trimethylsilyl)methyl)-2-diazo-*N*-((2*r*,5*r*)-2-phenyl-1,3-dioxan-5-yl)acetamide (40 mg, 0.10 mmol) in dry CH_2Cl_2 (4 mL) was added via cannula to a solution of $Rh_2(4R\text{-MEOX})_4$ (2.5 mol %) in dry CH_2Cl_2 (4 mL). After the addition was complete, the reaction mixture was heated at reflux for 20 min. The solvent was removed under reduced pressure to yield the title compound (35 mg, 0.094 mmol, 94%) as a white solid in 90% ee: mp 135–136°; IR (CH_2Cl_2) 3017, 2955, 1680, 1215, 849, 758 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.52–7.36 (m, 5H), 5.84 (s, 1H), 4.67 (dd, J = 14.0, 6.3 Hz, 1H), 4.26 (dd, J = 11.7, 5.3 Hz, 1H), 3.86 (dd, J = 11.7, 7.6 Hz, 1H), 3.70–3.66 (m, 1H), 2.77 (dd, J = 16.9, 6.5 Hz, 1H), 2.56 (dd, J = 16.9, 7.8 Hz, 1H), 2.10 (s, 1H), 0.18 (s, 9H), 0.12 (s, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 171.3, 137.5,

129.0, 128.5, 126.2, 95.6, 90.2, 67.1, 63.7, 34.1, 0.8, 0.2; HRMS (m/z): M^+ calcd for $C_{19}H_{31}NO_3Si_2$, 377.1843; found, 377.1847.



(*S*)-3-(2-(Benzyloxy)ethyl)-2-(3-methoxy-5-methylphenyl)-3-methylcyclopentanone [Synthesis of a Cyclopentanone from a Diazoketone].[308] Rh_2(*R*-PTTL)$_4$ (5 mg) was dissolved in toluene (2 mL). To this solution was added a solution of (*R*)-7-(benzyloxy)-1-diazo-1-(3-methoxy-5-methylphenyl)-5-methyl heptan-2-one (140 mg, 0.368 mmol) in toluene (2.0 mL) at rt within 1 min. The reaction was continued for an additional 15 min at rt. Then the reaction mixture was concentrated and the residue chromatographed to afford the title compound (108 mg, 0.305 mmol, 83%) as a mixture of two diastereomers: TLC R_f (PE/MTBE, 8 : 2) 0.22; IR (film) 2959, 1724, 1173, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 5H), 6.62 (s, 1H), 6.43 (m, 2H), 4.49 (s, 0.8H), 4.41 (s, 1.2H), 3.75 (s, 1.8H), 3.74 (s, 1.2H), 3.6–3.4 (m, 2H), 3.24 (s, 0.4H), 3.11 (s, 0.6H), 2.42 (m, 1H), 2.34 (s, 3H), 2.31 (m, 1H), 1.94 (m, 1H), 1.83 (m, 1H), 1.67 (m, 1H), 1.50 (m, 1H), 1.18 (s, 1.8H), 0.79 (s, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.9, 217.6, 159.4, 159.3, 139.1, 139.0, 138.3, 136.2, 135.9, 73.3, 73.2, 67.2, 67.0, 43.3, 43.2, 40.8, 36.1, 35.9, 33.8, 33.2, 32.3; d 128.5, 127.7, 123.9, 123.5, 113.6, 113.4, 113.3, 113.2, 68.9, 67.4, 55.2, 26.1, 21.8, 21.7, 20.7; HRMS (m/z): M^+ calcd for $C_{23}H_{28}O_3$, 352.2038; found, 352.2023.



(1*S*,2*R*)-cis-2-phenylcyclopentane-1-carboxylate [Synthesis of a Cyclopentane from a Methyl Diazoester].[309] Rh_2(*S*-PTTL)$_4$•2EtOAc (2.8 mg, 0.002 mmol, 0.01 equiv) was added to a solution of methyl 2-diazo-6-phenylhexanoate (46.5 mg, 0.20 mmol) in toluene (1.0 mL) at −78°. After 30 min, the mixture was concentrated at rt and the residue purified by column chromatography (silica gel, hexane/EtOAc = 15 : 1) to give the title compound (34.7 mg, 85%) as a colorless oil: R_f (hexane/EtOAc, 5 : 1) 0.39; $[\alpha]_D^{19}$ +98.88 (*c* 1.12, $CHCl_3$); IR (neat) 1732, 1200, 1171, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.15 (m, 5H, Ar*H*), 3.41 (ddd, J = 7.1, 9.0, 9.0 Hz, 1H, C1–*H*), 3.22 (s, 3H, CO_2CH_3), 3.16 (ddd, J = 6.2, 9.0, 9.0 Hz, 1H, C2–*H*), 2.15–1.95 (m, 5H), 1.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9 (C), 141.5 (C), 127.9 (CH), 127.8 (CH), 126.3 (CH), 50.9 (CH_3), 49.8 (CH), 49.2 (CH), 31.2 (CH_2), 28.6 (CH_2), 24.8

(CH_2); HRMS–EI (m/z): M^+ calcd for $C_{13}H_{16}O_2$, 204.1150; found, 204.1151. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.33; H, 7.98. The ee (95%) was determined by HPLC using a connected series of a Daicel Chiralcel OJ-H column and a Daicel Chiralpak AS-H column (hexanes/*i*-PrOH = 100 : 1, 1.0 mL/min): t_R [minor, (1*R*,2*S*)] = 12.9 min; t_R [major, (1*S*,2*R*)] = 14.7 min.

TABULAR SURVEY

The following tables are intended to include all reported examples of catalytic, asymmetric, intramolecular C–H insertion reactions reported up through and including 2009. The charts preceding the tables show the catalyst structures together with the bold numbers assigned to them. These numbers are used throughout the tables to reference the catalyst structures; note that the numbers differ from those used in the text portion of this chapter. Charts 1–4 provide a guide to the chiral dirhodium catalysts used in these reactions, and Chart 5 shows the chiral copper catalysts.

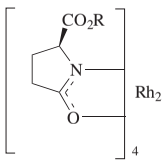
The arrangement of the Tabular Survey parallels that of the "Scope and Limitations" section. The organization of the entries in all of the tables is by ascending order of the carbon count of the substrate with the exclusion of protecting groups, esters (except for the carboxy carbon), and ethers, unless directly involved in the reaction. Isolated yields of the products are included in parentheses and a dash (–) indicates that no yield was reported.

The following abbreviations and acronyms (excluding those listed in "The *Journal of Organic Chemistry* Standard Abbreviations and Acronyms") are used in the Tabular Survey:

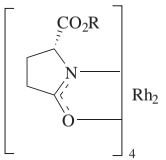
abs.	absolute
avg	average
BACIM	*tert*-butyl 1-acetyl-2-oxoimidazolidinate-4-carboxylate
BNAZ	benzyl 4-oxoazetidinate-2-carboxylate
BNOX	4-benzyl-1,3-oxazolidin-2-onate
BNP	1,1′-binaphthalene-2,2′-diyl hydrogen phosphate
BPPIM	isobutyl 2-oxo-1-(3-phenylpropanoyl)imidazolidinate-4-carboxylate
BPTA	2-(1,3-dioxo-1,3-dihydro-2*H*-benzo[f]isoindol-2-yl)propanoate
BPTPA	2-(1,3-dioxo-1,3-dihydro-2*H*-benzo[f]isoindol-2-yl)-3-phenylpropanoate
BPTTL	2-(1,3-dioxo-1,3-dihydro-2*H*-benzo[f]isoindol-2-yl)-3,3-dimethylbutanoate
BPTV	2-(1,3-dioxo-1,3-dihydro-2*H*-benzo[f]isoindol-2-yl)-3-methylbutanoate
BSP	1-(phenylsulfonyl)prolinate
BSPIM	methyl 2-oxo-1-[1-(phenylsulfonyl)prolyl]imidazolidinate-4-carboxylate

cap	caprolactamate
CHAZ	cyclohexyl 4-oxoazetidinate-2-carboxylate
dFIBAZ	*iso*-butyl 3,3-difluoro-4-oxoazetidinate-2-carboxylate
DOSP	(*p*-dodecylphenylsulfonyl)prolinato
ee	enantiomeric excess
EPPIM	ethyl 2-oxo-1-(3-phenylpropanoyl)imidazolidinate-4-carboxylate
IBAZ	isobutyl 4-oxoazetidinate-2-carboxylate
MACIM	methyl 1-acetyl-2-oxoimidazolidinate-4-carboxylate
MANIM	methyl 1-[methoxy(phenyl)acetyl]-2-oxoimidazolidinate-4-carboxylate
MBOIM	methyl 1-benzoyl-2-oxoimidazolidinate-4-carboxylate
MCHIM	methyl 1-(cyclohexylacetyl)-2-oxoimidazolidinate-4-carboxylate
MCPIM	methyl 2-oxo-1-[(2-*trans*-phenylcyclopropyl)carbonyl] imidazolidinate-4-carboxylate
MEAZ	methyl 4-oxoazetidinate-2-carboxylate
MEOX	methyl 2-oxo-1,3-oxazolidinate-4-carboxylate
MEPY	methyl 5-oxoprolinate
MNACIM	1-menthyl 4-methyl 2-oxoimidazolidinate-1,4-dicarboxylate
MPMT	2-({[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]oxy} carbonyl)benzoate
MPPIM	methyl 2-oxo-1-(3-phenylpropanoyl)imidazolidinate-4-carboxylate
NEPAZ	2,2-dimethylpropyl 4-oxoazetidinate-2-carboxylate
NEPY	2,2-dimethylpropyl 5-oxoprolinate
NTPA	2-(1,3-dioxo-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)-3-phenylpropanoate
NTTL	2-(1,3-dioxo-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)-3,3-dimethylbutanoate
ODPY	*n*-octadecyl 5-oxoprolinate
p-ABSA	*p*-acetamidobenzenesulfonyl azide
pfb	perfluorobutyrate
PCC	3-phenylcholestane-2-carboxylate
PHOX	4-phenyl-1,3-oxazolidin-2-onate
protos	1-[(4-methylphenyl)sulfonyl]prolinate
PTA	2-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)propanoate
PTAD	1-adamantyl(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)acetate
PTPA	2-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-3-phenylpropanoate
PTPG	(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)(phenyl)acetate
PTTL	2-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-3,3-dimethylbutanoate
PTV	2-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-3-methylbutanoate
TBDPS	*tert*-butyldiphenylsilyl
TBPRO	1-(*tert*-butylsulfonyl)prolinate
TBSP	1-[(4-*tert*-butylphenyl)sulfonyl]prolinate
TFEA	2,2,2-trifluoroethyl trifluoroacetate
THREOX	methyl (4*S*,5*R*)-5-methyl-2-oxo-1,3-oxazolidinate-4-carboxylate

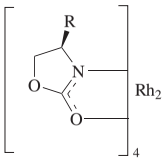
CHART 1. CHIRAL DIRHODIUM CARBOXAMIDATE CATALYSTS



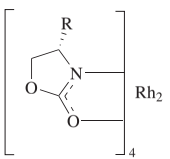
	R	
1a	Me	Rh_2(5*S*-MEPY)$_4$
1b	*n*-$C_{18}H_{37}$	Rh_2(5*S*-ODPY)$_4$



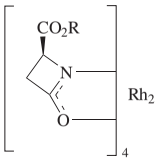
	R	
2a	Me	Rh_2(5*R*-MEPY)$_4$
2b	*t*-$BuCH_2$	Rh_2(5*R*-NEPY)$_4$



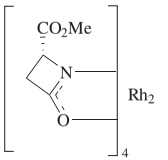
	R	
3a	MeO_2C	Rh_2(4*S*-MEOX)$_4$
3b	Ph	Rh_2(4*R*-PHOX)$_4$
3c	Bn	Rh_2(4*R*-BNOX)$_4$



	R	
4a	MeO_2C	Rh_2(4*R*-MEOX)$_4$
4b	Bn	Rh_2(4*R*-BNOX)$_4$

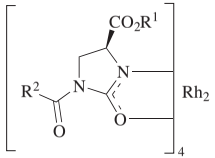


	R	
5a	Me	Rh_2(4*S*-MEAZ)$_4$
5b	*i*-Bu	Rh_2(4*S*-IBAZ)$_4$
5c	*c*-C_6H_{11}	Rh_2(4*S*-CHAZ)$_4$
5d	Bn	Rh_2(4S-BNAZ)$_4$
5e	*t*-$BuCH_2$	Rh_2(4S-NEPAZ)$_4$

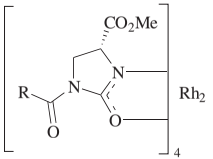


6 Rh_2(4*R*-MEAZ)$_4$

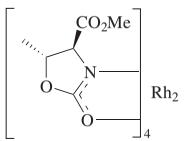
CHART 1. CHIRAL DIRHODIUM CARBOXAMIDATE CATALYSTS (*Continued*)



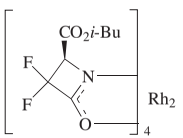
	R^1	R^2	
7a	Me	Me	Rh_2(4*S*-MACIM)$_4$
7b	Me	Ph	Rh_2(4*S*-MBOIM)$_4$
7c	Me	$PhCH_2CH_2$	Rh_2(4*S*-MPPIM)$_4$
7d	Me	*c*-$C_6H_{11}CH_2$	Rh_2(4*S*-MCHIM)$_4$
7e	Et	$PhCH_2CH_2$	Rh_2(4*S*-EPPIM)$_4$
7f	*i*-Bu	$PhCH_2CH_2$	Rh_2(4*S*-BPPIM)$_4$
7g	Me	(*S*)-Ph(OMe)CH	Rh_2(2′*S*,4*S*-MANIM)$_4$
7h	Me	(*R*)-Ph(OMe)CH	Rh_2(2′*R*,4*S*-MANIM)$_4$
7i	Me	(+)-menthyl	Rh_2(1′*S*,2′*R*,5′*S*,4*S*-MNACIM)$_4$
7j	Me	(−)-menthyl	Rh_2(1′*R*,2′*S*,5′*R*,4*S*-MNACIM)$_4$
7k	Me		Rh_2(2′*S*,3′*S*,4*S*-MCPIM)$_4$
7l	Me		Rh_2(2′*R*,3′*R*,4*S*-MCPIM)$_4$
7m	Me		Rh_2(2′*S*,4*S*-BSPIM)$_4$
7n	Me		Rh_2(2′*R*,4*S*-BSPIM)$_4$
7o	*t*-Bu	Me	Rh_2(4*S*-BACIM)$_4$



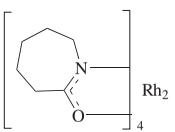
	R	
8a	Me	Rh_2(4*R*-MACIM)$_4$
8b	$PhCH_2CH_2$	Rh_2(4*R*-MPPIM)$_4$



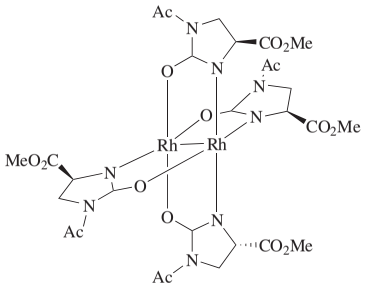
9 Rh_2(4*S*,5*R*-THREOX)$_4$



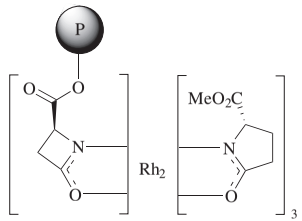
10 Rh_2(*S*-dFIBAZ)$_4$



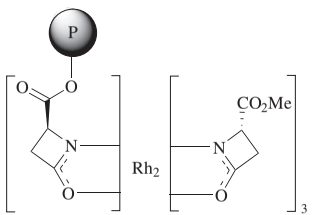
11 Rh_2(cap)$_4$



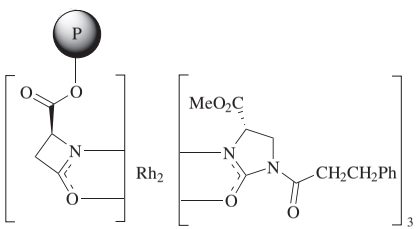
7a = 12 (1,3)-Rh_2(4*S*-MACIM)$_4$



13 N-AZ-Rh_2(5*S*-MEPY)$_3$

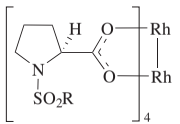


14 N-AZ-Rh_2(4*S*-MEAZ)$_3$

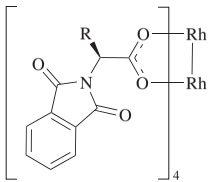


15 N-AZ-Rh_2(4*S*-MPPIM)$_3$

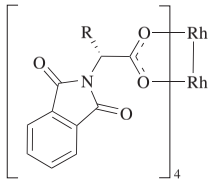
CHART 2. CHIRAL DIRHODIUM CARBOXYLATE CATALYSTS



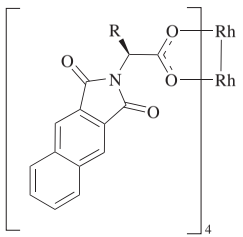
	R	
16a	*t*-Bu	Rh_2(*S*-TBPRO)$_4$
16b	*n*-dodecylC$_6$H$_4$	Rh_2(*S*-DOSP)$_4$
16c	Ph	Rh_2(*S*-BSP)$_4$
16d	4-*t*-BuC$_6$H$_4$	Rh_2(*S*-TBSP)$_4$
16e	1-Np	
16f	4-MeC$_6$H$_4$	Rh_2(protos)$_4$
16g	4-menthane-3-carboxylate	



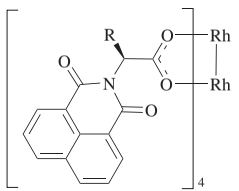
	R	
17a	Me	Rh_2(*S*-PTA)$_4$
17b	Bn	Rh_2(*S*-PTPA)$_4$
17c	*i*-Pr	Rh_2(*S*-PTV)$_4$
17d	*t*-Bu	Rh_2(*S*-PTTL)$_4$
17e	Ph	Rh_2(*S*-PTPG)$_4$
17f		Rh_2(*S*-PTAD)$_4$



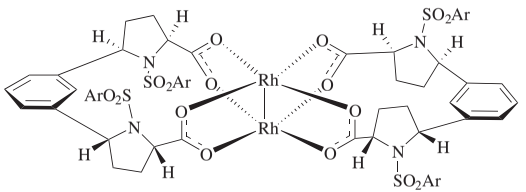
	R	
18a	Bn	Rh_2(*R*-PTPA)$_4$
18b		Rh_2(*R*-PTAD)$_4$



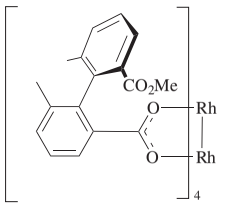
	R	
19a	Me	Rh_2(*S*-BPTA)$_4$
19b	Bn	Rh_2(*S*-BPTPA)$_4$
19c	*i*-Pr	Rh_2(*S*-BPTV)$_4$
19d	*t*-Bu	Rh_2(*S*-BPTTL)$_4$



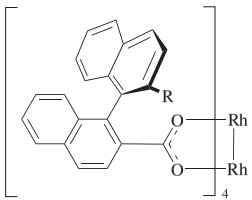
	R	
20a	*t*-Bu	Rh_2(*S*-NTTL)$_4$
20b	Bn	Rh_2(*S*-NTPA)$_4$



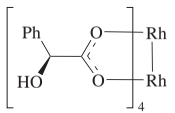
	Ar	
21a	2,4,6-(*i*-Pr)$_3$C$_6$H$_2$	Rh_2(*S*-biTISP)$_2$
21b	4-*t*-BuC$_6$H$_4$	



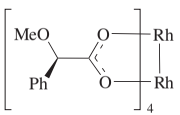
22



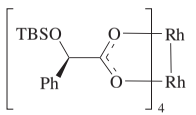
	R
23a	MeO_2C
23b	H



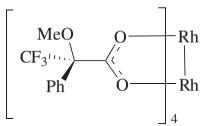
24 Rh_2(*S*-mandelate)$_4$



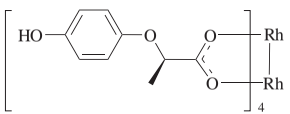
25 Rh_2(*R*-methoxymandelate)$_4$



26



27



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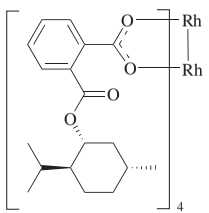
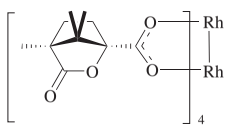
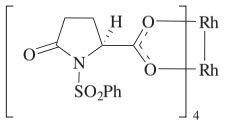


29 Rh_2(*S*-MPMT)$_4$

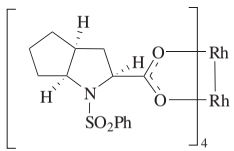


30 Rh_2(*S*-campha)$_4$

CHART 2. CHIRAL DIRHODIUM CARBOXYLATE CATALYSTS (*Continued*)



31



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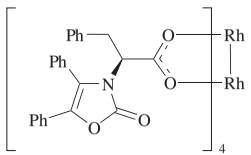

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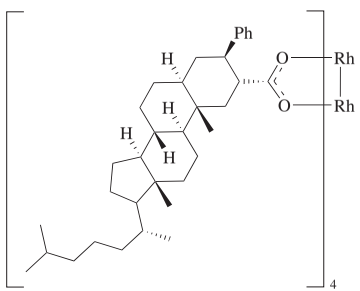
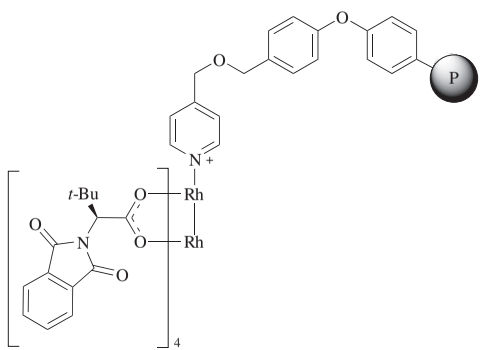
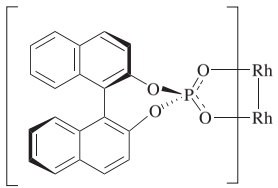


34 $Rh_2(PCC)_4$

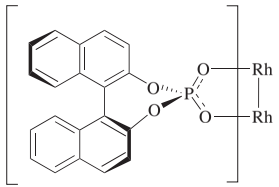


35

CHART 3. CHIRAL ARYLPHOSPHATE DIRHODIUM CATALYSTS



36 Rh_2(*S*-BNP)$_4$



37 Rh_2(*R*-BNP)$_4$

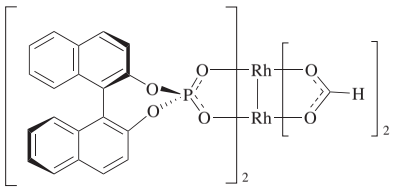


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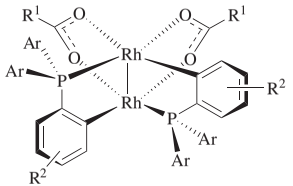
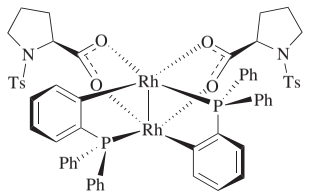
CHART 4. CHIRAL *cis*-ORTHOMETALATED ARYLPHOSPHINE DIRHODIUM CATALYSTS

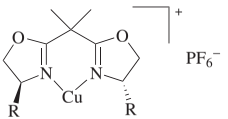


	Ar	R^1	R^2
39a	Ph	CF_3	H
39b	4-MeC_6H_4	CF_3	4-Me
39c	3-MeC_6H_4	CF_3	3-Me
39d	3,5-$Me_2C_6H_3$	CF_3	3,5-Me_2
39e	4-*t*-BuC_6H_4	CF_3	*t*-Bu
39f	4-FC_6H_4	CF_3	F
39g	Me	CF_3	H
39h	Ph		H

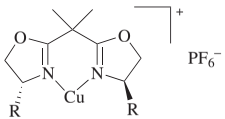


40

CHART 5. CHIRAL COPPER CATALYSTS



	R
41a	*i*-Pr
41b	*t*-Bu
41c	Ph



	R
42a	*t*-Bu
42b	Ph

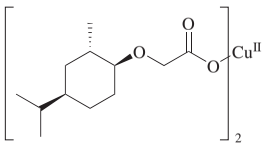


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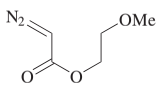
TABLE 1. MONOCYCLIC γ-LACTONES FROM DIAZOACETATES

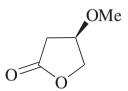
Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables, not to the text discussion, for structures indicated by the **bold** numbers.*

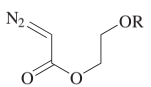
C_4



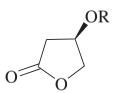
Catalyst, DCM



Cat.	Temp	Time (h)		% ee		Refs.
1a	reflux	6	(62)	91	(*S*)	258
1a	reflux	24	(—)	91	(*S*)	274
2a	reflux	6	(73)	91	(*R*)	258
3a	reflux	6	(65)	92	—	242
3c	reflux	24	(78)	55	(*R*)	274
4b	reflux	24	(—)	11	(*S*)	274
7a	reflux	6	(58)	58	—	242
7b	reflux	6	(56)	56	—	242
7c	reflux	6	(50)	50	—	242
7d	reflux	6	(63)	63	—	242
7k	reflux	6	(69)	91	—	244
7l	reflux	6	(64)	46	—	244
7m	reflux	6	(72)	94	—	244
7n	reflux	6	(72)	6	—	244
7i	35°	2	(66)	93	—	264
7j	35°	2	(75)	55	—	264

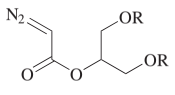


Catalyst, DCM, reflux, 6 h

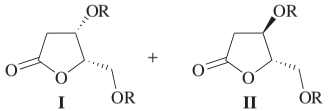


R	Cat.			% ee		Refs.
Et	**1a**	(64)	89	(*S*)		
Et	**2a**	(63)	89	(*R*)		258
Bn	**1a**	(64)	87	(*S*)		
Bn	**2a**	(69)	87	(*R*)		

C_5



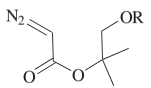
Catalyst, DCM, reflux, 10 h



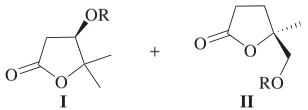
I + **II** (65–81) 153, 154

R	Cat.	**I**/**II**	% ee **I**		% ee **II**	
Me	**2a**	93:7	97	(3*R*,4*R*)	50	(3*S*,4*R*)
Me	**1a**	94:6	97	(3*S*,4*S*)	45	(3*R*,4*S*)
Me	**3a**	91:9	98	(3*S*,4*S*)	76	(3*R*,4*S*)
Et	**2a**	93:7	89	(3*R*,4*R*)	50	(3*S*,4*R*)
Et	**1a**	94:6	90	(3*S*,4*S*)	45	(3*R*,4*S*)
Et	**3a**	91:9	96	(3*S*,4*S*)	85	(3*R*,4*S*)
Bn	**2a**	93:7	94	(3*R*,4*R*)	50	(3*S*,4*R*)
Bn	**1a**	93:7	94	(3*S*,4*S*)	—	(3*R*,4*S*)
Bn	**3a**	90:10	94	(3*S*,4*S*)	—	(3*R*,4*S*)

C_6

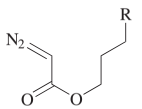
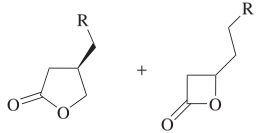
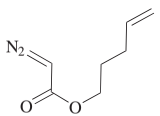
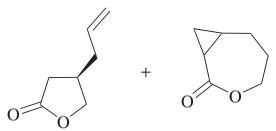
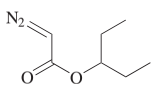
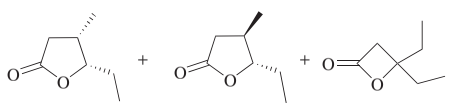


Catalyst, DCM, reflux, 6 h



R	Cat.	**I** + **II**	**I**/**II**	% ee **I**		
Me	**1a**	(68)	—	56	(*S*)	258
Me	**2a**	(70)	—	57	(*R*)	258
Me	**7a**	(85)	87:13	56	(*S*)	261
Bn	**1a**	(85)	—	51	(*S*)	258
Bn	**7a**	(74)	84:16	58	(*S*)	261

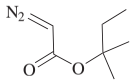
TABLE 1. MONOCYCLIC γ-LACTONES FROM DIAZOACETATES (*Continued*)

Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{6–8}$ 	Catalyst **7c**, DCM, reflux, 10 h	 **I** + **II**	259
C_7 	Catalyst, DCM, reflux	 **I** **I + II** (<50) **II**	313
	Catalyst, DCM, reflux, 12 h	 **I** **II** **III**	152
			152
			152
			152
			152
			242

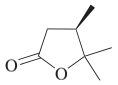
R	I	% ee I		II
Me	(52)	96	(*S*)	(4)
i-Pr	(60)	95	(*S*)	(5)

Cat.	I/II	% ee I
$Rh_2(OAc)_4$	<1:99	—
16d	<1:99	—
5b	8:92	—
1a	42:58	93
7c	47:53	98
3a	19:81	98
41b	<1:99	—

Cat.	I + II + III	I/II/III	% ee I	% ee II
1a	(75)	73:20:7	98	71
3a	(86)	60:27:13	98	92
7a	(83)	92:5:3	86	36
7c	(85)	92:3:5	99	—
7d	(90)	95:2:3	99	—
7b	(88)	83:9:8	81	—

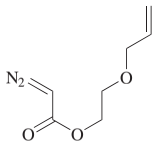


Catalyst, DCM, reflux, 6 h

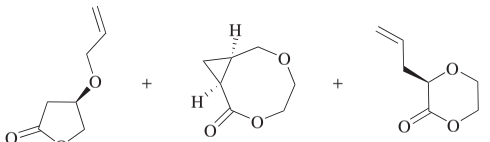


Cat.		% ee
1a	(54)	0
3a	(42)	21
7a	(47)	62

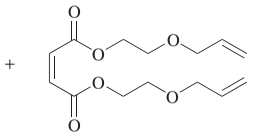
261



Catalyst, DCM, reflux, 2.5 h



I **II** **III**

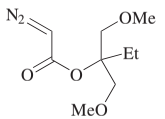
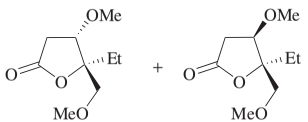
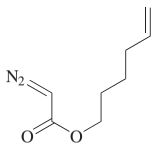
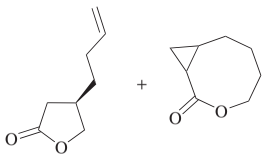


IV

315

Cat.	**I + II + III + IV**	**I/II/III/IV**	% ee **I**	% ee **II**	% ee **III**
$Rh_2(OAc)_4$	(93)	15:70:6:9	—	—	—
$Cu(MeCN)_4PF_6$	(87)	0:9:25:66	—	—	—
41b	(61)	3:2:7:88	22	67	6
41b[a]	(61)	9:5:60:26	27	71	8
16a	(50)	5:84:7:4	19	28	18
10	(34)	13:12:17:58	62	19	88
5b	(63)	77:4:0:19	91	49	—
1a	(64)	98:0:0:2	91	—	—
4a	(78)	97:0:2:1	96	—	94

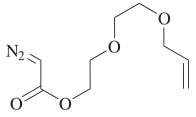
TABLE 1. MONOCYCLIC γ-LACTONES FROM DIAZOACETATES (*Continued*)

	Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		Catalyst, DCM, reflux, 10 h	 **I** + **II** **I**: 34–72% ee **II**: 34–72% ee	154
C_8		Catalyst, DCM, reflux	 **I** + **II** (<50) + **II**	313

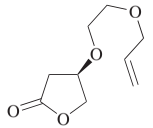
Cat.	**I** + **II**	**I**/**II**
$Rh_2(OAc)_4$	(86)	76:24
2a	(79)	60:40
3a	(61)	64:36
7a	(82)	55:45

Cat.	**I**/**II**	% ee **I**
$Rh_2(OAc)_4$	16:84	—
16a	18:82	10
5b	50:50	50
1a	86:14	95
7c	87:13	>97
3a	19:81	97
41b	<1:99	74

C_9

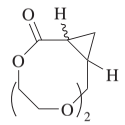


Catalyst, DCM, reflux, 2.5 h



I

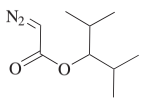
+



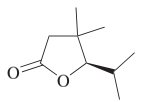
II

315

Cat.	**I** + **II**	**I**/**II**	**II**	*cis*/*trans*	% ee **I**	% ee *cis*-**II**	% ee *trans*-**II**
$Rh_2(OAc)_4$	(83)	4:96		87:13	—	—	—
$Cu(MeCN)_4PF_6$	(64)	0:100		91:9	—	—	—
41b	(58)	0:100		86:14	—	79	85
16a	(80)	2:98		87:13	14	11	12
10	(67)	15:85		84:16	75	33	67
5b	(69)	58:42		88:12	90	56	64
1a	(77)	95:5		88:12	92	53	65
3a	(73)	99:1		88:12	92	48	67



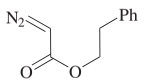
Catalyst, DCM, rt, 20 h



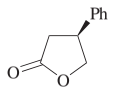
Cat.		% ee
1a	(42)	92
2a	(42)	95

155

C_{10}

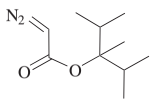


Catalyst, DCM, reflux, 6 h

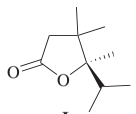


Cat.		% ee	
1a	(42)	46	(*R*)
2a	(34)	45	(*S*)

258

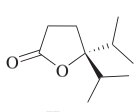


Catalyst, DCM, reflux, 6 h



I

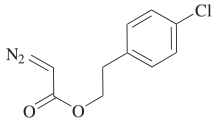
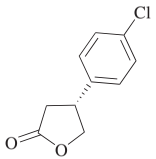
+



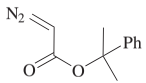
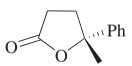
II

Cat.	**I** + **II**	**I**/**II**	% ee **I**	
1a	(77)	93:7	61	258
2a	(77)	—	60	258
2b	(82)	—	70	258
3a	(70)	70:30	0	261
7a	(73)	83:17	85	261

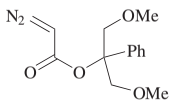
TABLE 1. MONOCYCLIC γ-LACTONES FROM DIAZOACETATES (*Continued*)

Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Catalyst, DCM, reflux, 5 h		328

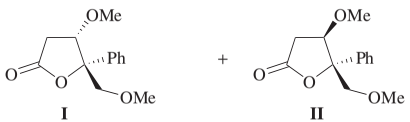
Cat.		% ee	
7c	(81)	95	(*R*)
2a	(13)	51	(*S*)
3a	(67)	45	(*S*)

C_{11} 	Catalyst, DCM, reflux, 6 h		258

Cat.		% ee	
1a	(30)	76	(*R*)
2a	(39)	79	(*S*)



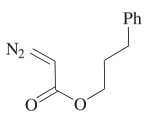
Catalyst, DCM, reflux, 10 h



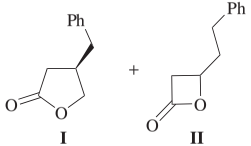
I + **II**

Cat.	**I** + **II**	**I**/**II**	% ee **I**	% ee **II**
$Rh_2(OAc)_4$	(59)	83:17	—	—
2a	(72)	67:33	34–72	34–72
3a	(76)	63:37	34–72	34–72
7a	(42)	60:40	34–72	34–72
11	(35)	66:35	—	—

154



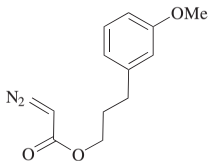
Catalyst, DCM, reflux, 13 h



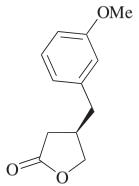
I + **II**

Cat.	**I** + **II**	**I**/**II**	% ee **I**	
2a	(49)	93:7	72	(*R*)
3a	(76)	94:6	51	(*S*)
7c	(59)	93:7	87	(*S*)
8b	(76)	93:7	91	(*R*)

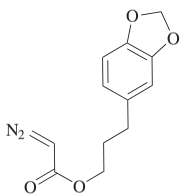
259



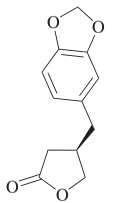
Catalyst, DCM, reflux, 10 h



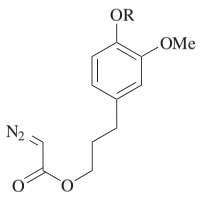
Cat.		% ee		
3a	(56)	45	(*R*)	259
2a	(66)	68	(*S*)	223
7a	(25)	84	(*S*)	223
7c	(66)	91	(*S*)	223
8b	(63)	93	(*R*)	223



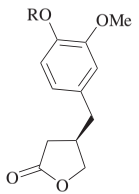
Catalyst, DCM, reflux, 13 h



Cat.		% ee		
7c	(67)	95	(*S*)	259
8b	(57)	95	(*R*)	

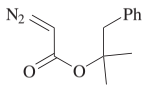
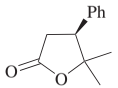
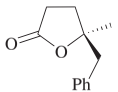


Catalyst, DCM, reflux, 10 h

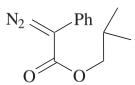
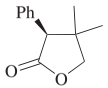


R	Cat.	Time (h)				
Me	**7c**	10	(62)	94	(*S*)	259
Me	**8b**	10	(61)	94	(*R*)	259
Bn	**8b**	10	(59)	96.5	(*R*)	259
TBDPS	**7c**	5	(68)	93	(*S*)	260
TBDPS	**2a**	5	(51)	67	(*R*)	260
TBDPS	**3a**	5	(37)	36	(*S*)	260
TBDPS	**5b**	5	(40)	42	(*S*)	260

TABLE 1. MONOCYCLIC γ-LACTONES FROM DIAZOACETATES (*Continued*)

Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	Catalyst, DCM, reflux, 6 h	 **I** +  **II**	261

Cat.	I + II	I/II	% ee I	% ee II
1a	(62)	30:70	53	70
3a	(75)	20:80	34	10
7a	(74)	32:68	77	83

	Catalyst, reflux		Cat.	Solvent		% ee	143
			$Rh_2(OAc)_4$	DCM	(79)	—	
			6	DCM	(94)	90	
			5b	DCM	(89)	84	
			16b	DCM	(95)	56	
			16b	pentane	(89)	86	

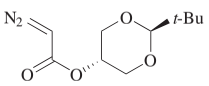
[a] The catalyst was diluted by a factor of 20.

TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES

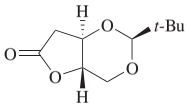
Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables, not to the text discussion, for structures indicated by the **bold** numbers.*

C_5



Catalyst, DCM, reflux, 6 h



Cat.		% ee
5b	(35)	81
3a	(42)	59
1a	(49)	52

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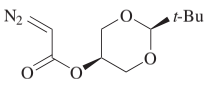
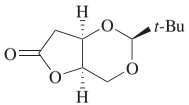


Catalyst, DCM, reflux, 6 h



Cat.		% ee
5b	(32)	85
3a	(57)	96
4a	(55)	96
7c	(59)	91

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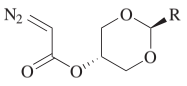
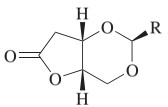


Catalyst, DCM, reflux, 6 h



R	Cat.		% ee
Ph	**5b**	(85)	88
Ph	**3a**	(48)	67
Ph	**1a**	(71)	94
Ph	**2a**	(75)	94
2-Np	**3a**	(68)	83
2-Np	**1a**	(72)	95

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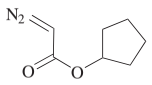
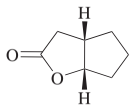
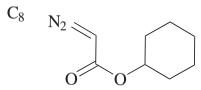
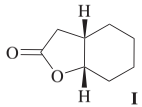
TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES (*Continued*)

Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)					Refs.
C_7 	Catalyst, DCM						
		Cat.	Temp	Time (h)	% ee		
		1a	rt	20 (25)	38	(3*S*,6*S*)	155
		1a	reflux	12 (54)	40	—	152
		2a	rt	20 (25)	38	(3*R*,6*R*)	155
		3c	rt	20 (15)	3	—	155
		7a	reflux	12 (40)	89	—	152
		7c	reflux	6 (67)	93	—	244
		7k	reflux	6 (81)	88	—	244
		7l	reflux	6 (75)	40	—	244
		7m	reflux	6 (78)	98	—	244
		7n	reflux	6 (62)	22	—	244
		7i	reflux	2 (84)	33	—	264
		7j	reflux	2 (79)	77	—	264

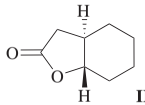


Catalyst, DCM



I

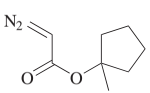
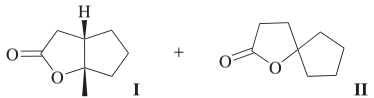
+



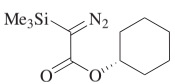
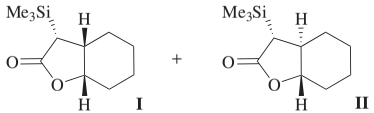
II

Cat.	Temp	Time (h)	**I + II**	**I/II**	% ee **I**		% ee **II**		
$Rh_2(OAc)_4$	rt	20	(46)	40:60	—	—	—	—	155
$Rh_2(OAc)_4$	reflux	10	(70)	40:60	—	—	—	—	243
1a	rt	20	(30)	75:25	95	(3*S*,7*S*)	90	(3*S*,7*R*)	155
1a	—	—	(68–80)	86:14	>99	—	93	—	263
1b	—	—	(68–80)	74:26	99	—	95	—	263
2a	rt	20	(30)	75:25	97	(3*R*,7*R*)	—	(3*R*,7*S*)	155
2a	reflux	10	(65)	75:25	97	—	91	—	243
3a	reflux	10	(50)	55:45	96	—	95	—	243
3b	rt	20	(5)	—	—	—	—	(3*R*,7*S*)	155
3c	rt	20	(30)	33:67	60	(3*R*,7*R*)	60	(3*R*,7*S*)	155
7a	reflux	10	(70)	99:1	97	(3*S*,7*S*)	63	(3*S*,7*R*)	243
7c	reflux	6	(71)	100:0	92	—	—	—	244
7e	reflux	—	(57)	84:16	88	—	37	—	251
7f	reflux	—	(69)	78:22	88	—	73	—	251
7g	reflux	16	(60)	87:13	82	(3*S*,7*S*)	56	(3*S*,7*R*)	262
7h	reflux	16	(68)	72:28	80	(3*S*,7*S*)	72	(3*S*,7*R*)	262
7i	35°	2	(80)	100:0	95	—	—	—	264
7j	35°	2	(71)	79:21	84	—	68	—	264
7k	reflux	6	(78)	99:1	97	—	—	—	244
7l	reflux	6	(63)	80:20	72	—	13	—	244
7m	reflux	6	(88)	97:3	>99	—	>99	—	244
7n	reflux	6	(89)	98:2	74	—	33	—	244
7o	reflux	—	(82)	99:1	99	—	64	—	251
13	—	—	(68–80)	54:46	97	—	89	—	263
15	—	—	(68–80)	60:40	95	—	93	—	263

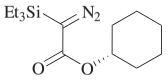
TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES (*Continued*)

Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	Catalyst, DCM	 **I** + **II**	

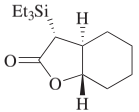
Cat.	Temp	Time (h)	**I** + **II**	**I**/**II**	% ee **I**	
1a	rt	20	(30)	—	31	155
1a	reflux	6	(52)	94:6	36	261
2a	rt	20	(30)	—	36	155
3a	reflux	6	(61)	83:17	33	261
3c	rt	20	(17)	—	1	155
7a	reflux	6	(56)	90:10	85	261

	Catalyst, toluene, rt	 **I** + **II**	256

Cat.	Time (h)	**I** + **II**	**I**/**II**	% ee **I**	% ee **II**
17d	2.5	(82)	21:79	27	31
20a	1	(83)	20:80	0	33



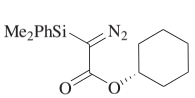
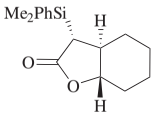
Catalyst, Solvent



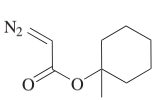
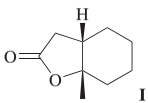
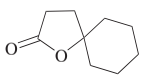
256

Cat.	Solvent	Temp	Time (h)		% ee
$Rh_2(OAc)_4$	benzene	reflux	15	(42)	—
$Rh_2(OAc)_4$	toluene	rt	96	(33)	—
$Rh_2(OAc)_4$	DCM	rt	24	(61)	—
ent-**22**	benzene	reflux	21	(21)	39
1a	benzene	reflux	48	(16)	0
3a	benzene	reflux	6	(0)	—
5d	benzene	reflux	5	(10)	71
5d	DCE	reflux	20	(11)	74
5d	toluene	reflux	4	(4)	79
5d	$PhCF_3$	reflux	3	(7)	62
16b	benzene	reflux	1.5	(49)	13
16d	benzene	reflux	1.5	(45)	13
17b	benzene	reflux	2	(50)	19
17b	$PhCF_3$	reflux	3	(48)	16
17d	benzene	60°	1	(67)	60
17d	toluene	rt	1.5	(75)	64
19d	toluene	rt	1	(74)	66
20a	benzene	reflux	15	(68)	59
20a	benzene	rt	2.5	(82)	62
20a	DCM	reflux	1	(87)	56
20a	DCM	rt	2	(90)	56
20a	toluene	rt	1.5	(76)	61
36	benzene	reflux	2.5	(30)	40
29	benzene	40°	2.5	(34)	7
30	benzene	reflux	15	(62)	2

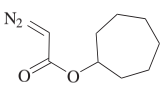
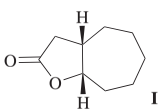
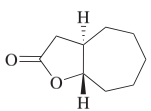
TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES (*Continued*)

Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	Catalyst, toluene		256

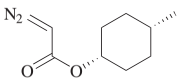
Cat.	Temp	Time (h)		% ee
$Rh_2(OAc)_4$	reflux	2	(29)	—
20a	rt	48	(34)	41
17d	reflux	2	(27)	42
19d	reflux	2.5	(4)	43

C_9 	Catalyst, DCM	 **I** +  **II**	

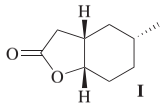
Cat.	Temp	Time (h)	**I + II**	**I/II**	% ee **I**	
1a	rt	20	(30)	—	74	155
1a	reflux	6	(63)	90:10	75	261
2a	rt	20	(30)	—	66	155
3a	reflux	6	(60)	78:22	40	261
3c	rt	20	(30)	—	44	155
7a	reflux	6	(68)	90:10	90	261
7a	reflux	18	(68)	90:10	90	242
12	reflux	18	(49)	91:9	53	242

	Catalyst, DCM, reflux, 10 h	 **I** +  **II**	247

Cat.	**I + II**	**I/II**	% ee **I**	% ee **II**
$Rh_2(OAc)_4$	(29)	30:70	—	—
2a	(80)	71:29	96	85
3a	(68)	58:42	97	94
7a	(75)	99:1	96	61

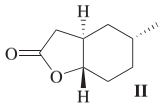


Catalyst, DCM, reflux, 10 h



I

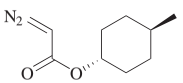
+



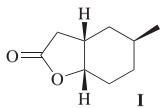
II

243

Cat.	**I** + **II**	**I**/**II**	% ee **I**	% ee **II**
2a	(—)	98:2	98	84
3a	(—)	>99:1	98	—
7a	(—)	>99:1	95	—

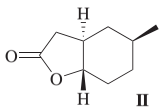


Catalyst, DCM, reflux, 10 h



I

+

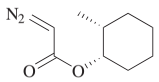
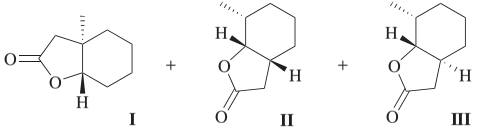
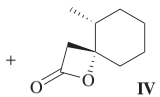


II

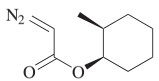
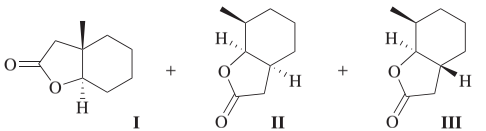
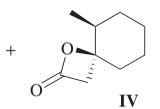
243

Cat.	**I** + **II**	**I**/**II**	% ee **I**	% ee **II**
2a	(—)	15:85	82	91
3a	(—)	10:90	68	95
7a	(—)	63:37	93	57

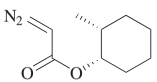
TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES (*Continued*)

Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	Catalyst, DCM, reflux, 11 h	 **I** + **II** + **III** +  **IV**	134

Cat.	I + II + III + IV	I/II/III/IV
1a	(95)	94:1:0:5
2a	(79)	4:91:3:2
3a	(82)	90:1:0:9
4a	(91)	2:88:7:3
7c	(46)	28:16:0:56
8b	(88)	0:98:0:2

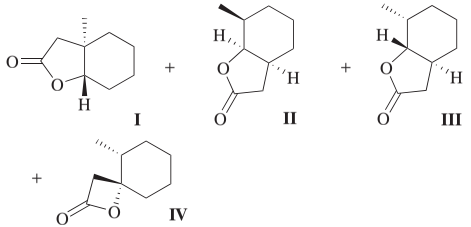
	Catalyst, DCM, reflux, 11 h	 **I** + **II** + **III** +  **IV**	134

Cat.	I + II + III + IV	I/II/III/IV
1a	(86)	5:90:3: 2
2a	(74)	92:3:0: 5
3a	(89)	2:88:7: 3
4a	(86)	88:3:0: 9
7a	(90)	1:96:1:2
7c	(91)	0:98:0: 2



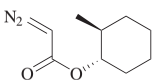
racemic

Catalyst, DCM, reflux, 11 h

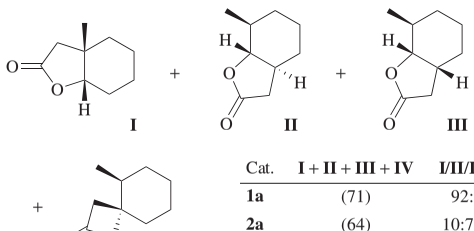


266

Cat.	I + II + III + IV	I/II/III/IV	% ee I	% ee II	% ee IV
1a	(75)	45:49:2:4	91	98	4
2a	(62)	44:49:2:5	92	98	5
3a	(86)	40:47:4:9	99	99	9
7a	(77)	11:66:1:22	87	77	22



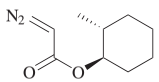
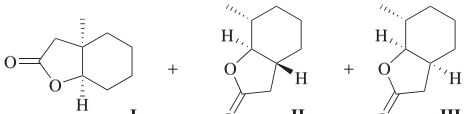
Catalyst, DCM, reflux, 11 h



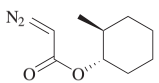
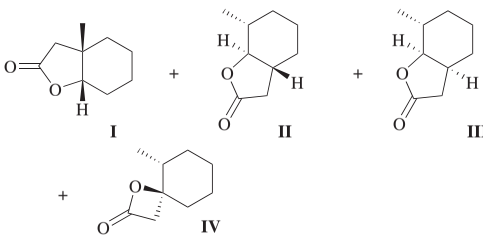
134

Cat.	I + II + III + IV	I/II/III/IV
1a	(71)	92:3:2:3
2a	(64)	10:74:16:0
3a	(77)	87:3:1:9
4a	(86)	2:87:9:2
7c	(69)	58:9:7:26
11	(12)	56:38:6:0

TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES (*Continued*)

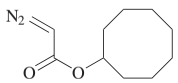
Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	Catalyst, DCM, reflux, 11 h	 **I** + **II** + **III** + **IV**	134

Cat.	I + II + III + IV	I/II/III/IV
1a	(75)	13:72:15:0
2a	(56)	88:6:3:3
3a	(92)	4:85:9:2
4a	(74)	84:4:3:9
7c	(81)	3:21:76:0

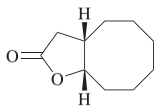
 racemic	Catalyst, DCM, reflux, 11 h	 **I** + **II** + **III** + **IV**	266

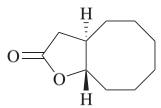
Cat.	I + II + III + IV	I/II/III/IV	% ee I	% ee II	% ee III
1a	(65)	49:40:9:2	80	93	78
2a	(57)	47:41:9:3	79	93	82
3a	(75)	39:50:6:5	96	95	79
7a	(57)	18:19:51:12	87	49	86

C_{10}



Catalyst, DCM, reflux, 10 h



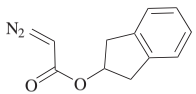
I + 

II

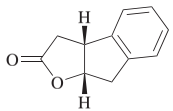
243

Cat.	**I** + **II**	**I**/**II**	% ee **I**	% ee **II**
$Rh_2(OAc)_4$	(33)	29:71	—	—
2a	(80)	72:28	97	59
3a	(60)	57:43	99	95
7a	(62)	99:1	97	95

C_{11}



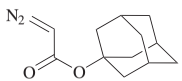
Catalyst, DCM, reflux, 12 h



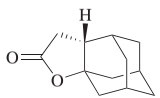
Cat.		% ee
1a	(35)	36
7a	(20)	79
7c	(75)	92

152

C_{12}

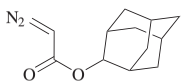


Catalyst **3a**, DCM, reflux, 10 h

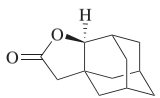


(86) 90% ee

247



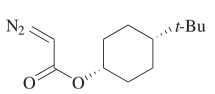
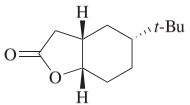
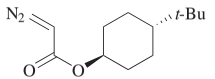
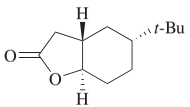
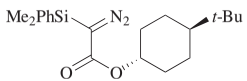
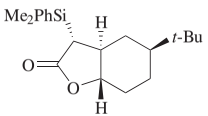
Catalyst, DCM, reflux, 10 h



Cat.		% ee
3a	(82)	98
1a	—	88

247

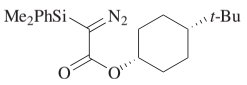
TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES (*Continued*)

Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	Catalyst, DCM, reflux, 20 h		155
	Catalyst, DCM, reflux, 20 h		155
	Catalyst, Solvent		256

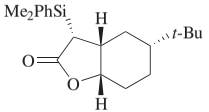
Cat.		% ee
1a	(40)	95
2a	(40)	96

Cat.		% ee
1a	(30)	94
2a	(30)	95

Cat.	Solvent	Temp	Time (h)		% ee
$Rh_2(OAc)_4$	benzene	reflux	15	(34)	—
5d	benzene	reflux	2	(16)	64
37	benzene	reflux	2	(18)	24
17b	benzene	reflux	2	(7)	2
17d	toluene	rt	2	(73)	77
20a	toluene	rt	2	(73)	78
19d	toluene	rt	2	(63)	69

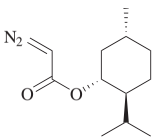


Catalyst, Solvent

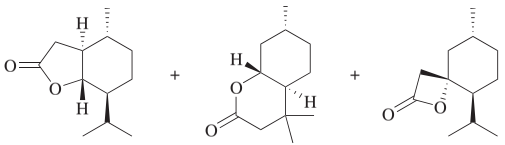


256

Cat.	Solvent	Temp	Time (h)		% ee
$Rh_2(OAc)_4$	benzene	reflux	15	(21)	—
5d	benzene	reflux	2	(5)	43
17b	benzene	reflux	2	(23)	13
17d	toluene	rt	2	(50)	43
20a	toluene	rt	2	(28)	66
19d	toluene	rt	2	(42)	8



Catalyst, DCM, reflux, 11 h

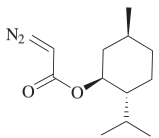
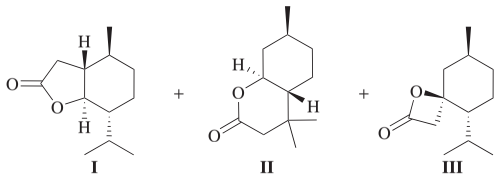


I **II** **III**

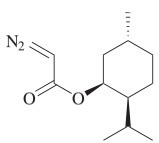
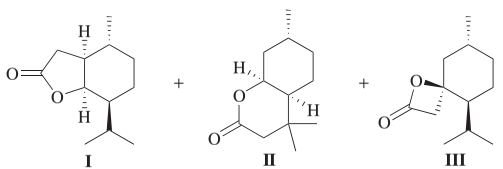
134

Cat.	**I + II + III**	**I/II/III**
$Rh_2(OAc)_4$	(17)	56:44:0
11	(33)	56:44:0
1a	(85)	73:27:0
2a	(84)	42:58:0
3a	(87)	100:0:0
4a	(84)	28:50:22
7c	(72)	73:27:0
5d	(63)	93:7:0
5b	(61)	95:5:0
41b	(15)	93:7:0

TABLE 2. SILYLATIVE TRANSFORMATIONS OF PROCHIRAL CYCLIC KETONES (*Continued*)

Cyclic Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	Catalyst, DCM, reflux, 11 h	 **I** **II** **III**	134

Cat.	I + II + III	I/II/III
1a	(70)	44:56:0
2a	(92)	75:25:0
3a	(61)	29:53:18
4a	(75)	100:0:0
7c	(50)	77:23:0
41b	(28)	97:3:0

	Catalyst, DCM, reflux, 11 h	 **I** **II** **III**	134

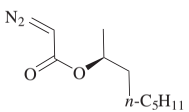
Cat.	I + II + III	I/II/III
$Rh_2(OAc)_4$	(16)	51:49:0
11	(26)	55:45:0
1a	(65)	52:45:3
2a	(75)	89:11:0
3a	(77)	28:39:33
4a	(97)	98:2:0
41b	(84)	94:6:0

TABLE 3. β-LACTONES FROM DIAZOACETATES

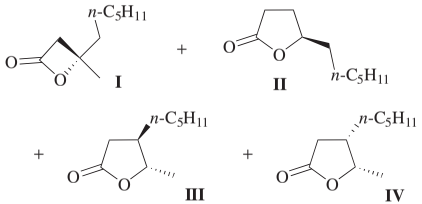
Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables, not to the text discussion, for structures indicated by the **bold** numbers.*

C_{10}

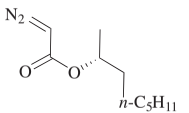


Catalyst, DCM, reflux, 11 h

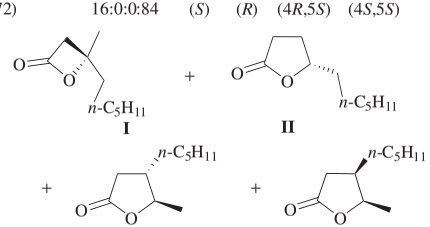


I **II** **III** **IV**

Cat.	I + II + III + IV	I/II/III/IV	I	II	III	IV	
2a	(52)	65:14:14:7	(*S*)	(*R*)	(4*R*,5*S*)	(4*S*,5*S*)	266
4a	(53)	85:9:4:2	(*S*)	(*R*)	(4*R*,5*S*)	(4*S*,5*S*)	266
7a	(74)	22:0:2:76	(*S*)	(*R*)	(4*R*,5*S*)	(4*S*,5*S*)	266
7c	(72)	16:0:0:84	(*S*)	(*R*)	(4*R*,5*S*)	(4*S*,5*S*)	134



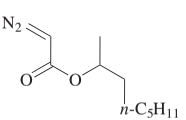
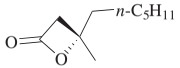
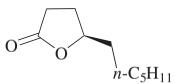
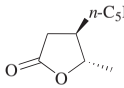
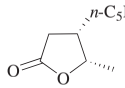
Catalyst, DCM, reflux, 11 h



I **II** **III** **IV**

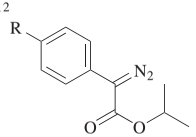
Cat.	I + II + III + IV	I/II/III/IV	I	II	III	IV	
1a	(59)	66:14:14:6	(*R*)	(*S*)	(4*S*,5*R*)	(4*R*,5*R*)	266
2a	(53)	43:1:14:42	(*R*)	(*S*)	(4*S*,5*R*)	(4*R*,5*R*)	266
3a	(59)	83:10:4:2	(*R*)	(*S*)	(4*S*,5*R*)	(4*R*,5*R*)	266
4a	(71)	57:2:12:29	(*R*)	(*S*)	(4*S*,5*R*)	(4*R*,5*R*)	266
7a	(58)	39:44:7:10	(*R*)	(*S*)	(4*S*,5*R*)	(4*R*,5*R*)	266
7c	(55)	21:61:5:13	(*R*)	(*S*)	(4*S*,5*R*)	(4*R*,5*R*)	134

TABLE 3. β-LACTONES FROM DIAZOACETATES (*Continued*)

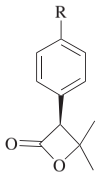
Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Catalyst, DCM, reflux, 11 h	 **I** +  **II** +  **III** +  **IV**	266

Cat.	**I** + **II** + **III** + **IV**	**I**/**II**/**III**/**IV**	% ee **I**	**I**	% ee **II**	**II**	% ee **III**	**III**	% ee **IV**	**IV**
1a	(50)	49:7:17:27	16	(*R*)	88	(*R*)	6	(4*R*,5*S*)	74	(4*S*,5*S*)
2a	(45)	85:9:4:2	17	(*S*)	87	(*S*)	5	(4*S*,5*R*)	77	(4*R*,5*R*)
3a	(59)	22:0:2:76	10	(*R*)	93	(*R*)	51	(4*R*,5*S*)	88	(4*S*,5*S*)
7a	(65)	16:0:0:84	15	(*R*)	98	(*R*)	64	(4*R*,5*S*)	80	(4*S*,5*S*)

C_{11-12}

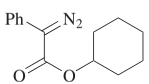


Catalyst, Solvent, reflux

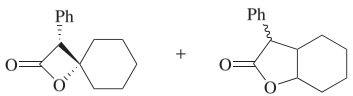


R	Cat.	Solvent		% ee	
H	$Rh_2(OAc)_4$	DCM	(84)	—	143
H	**1a**	DCM	(0)	—	263
H	**13**	DCM	(71)	42	263
H	**7c**	DCM	(0)	—	263
H	**15**	DCM	(74)	39	263
H	**5a**	DCM	(83)	33	143
H	**14**	DCM	(83)	28	263
H	**5b**	DCM	(79)	26	143
H	**5d**	DCM	(66)	30	143
H	**5c**	DCM	(85)	35	143
H	**5e**	DCM	(84)	24	143
H	**16b**	DCM	(86)	36	143
H	**16b**	pentane	(78)	41	143
MeO	**16b**	pentane	—	33	143
Me	**5a**	DCM	(74)	48	143
Me	**16b**	pentane	(34)	27	143

C_{14}



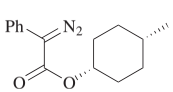
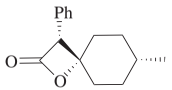
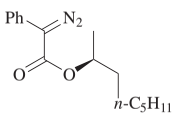
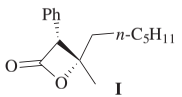
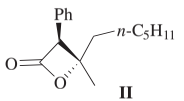
Catalyst, Solvent, reflux



I + **II** 143

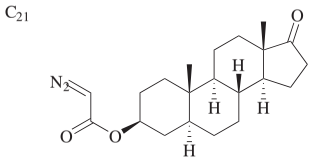
Cat.	Solvent	**I** + **II**	**I**/**II**	% ee **I**
$Rh_2(OAc)_4$	DCM	(55)	98:2	—
5a	DCM	(67)	98:2	50
5b	DCM	(66)	97:3	51
5e	DCM	(65)	97:3	42
16b	DCM	(52)	98:2	49
16b	pentane	(69)	98:2	63

TABLE 3. β-LACTONES FROM DIAZOACETATES (*Continued*)

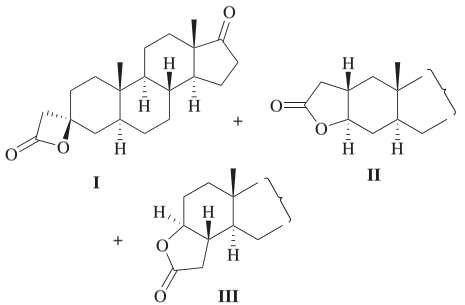
Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	Catalyst, Solvent, reflux		143
C_{16} 	Catalyst, Solvent, reflux	 **I** +  **II**	143

Cat.	Solvent		% ee
5a	DCM	(74)	44
16b	pentane	(56)	44

Cat.	Solvent	**I + II**	**I/II**
$Rh_2(OAc)_4$	DCM	(91)	37:63
5a	DCM	(79)	22:78
6	DCM	(60)	53:47
5b	DCM	(68)	36:64
16b	pentane	(56)	69:31



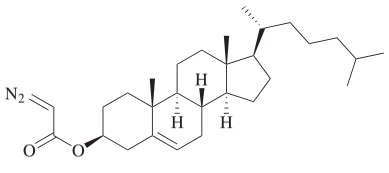
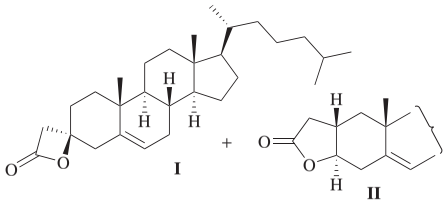
Catalyst, DCM, reflux



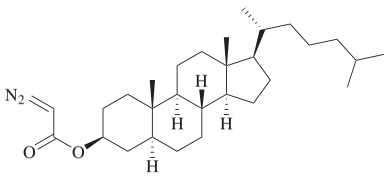
135

Cat.	Time (h)	**I + II + III**	**I/II/III**
$Rh_2(OAc)_4$	2.5	(62)	32:22:46
2a	5.5	(84)	23:73:4
1a	5.5	(83)	65:3:32
4a	5.5	(89)	37:60:3
3a	5.5	(86)	87:3:10
5a	5.5	(76)	42:1:57

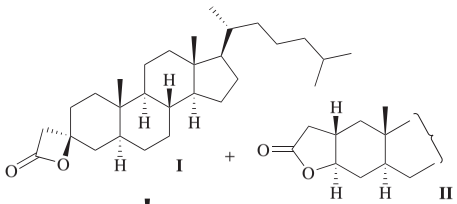
TABLE 3. β-LACTONES FROM DIAZOACETATES (*Continued*)

Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29} 	Catalyst, DCM, reflux	 **I** + **II**	135

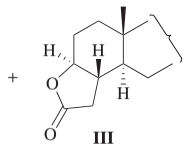
Cat.	Time (h)	I + II	I/II
$Rh_2(OAc)_4$	2.5	(<5)	—
2a	5.5	(81)	6:94
1a	5.5	(74)	67:33
4a	5.5	(81)	11:89
3a	5.5	(80)	90:10
5a	5.5	(69)	73:27
5b	5.5	(31)	68:32
7c	5.5	(54)	80:20
41c	5.5	—	28:72
42b	5.5	—	63:37



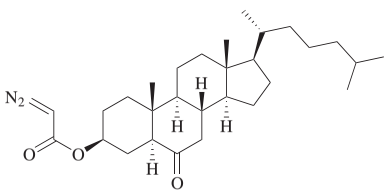
Catalyst, DCM, reflux, 5.5 h



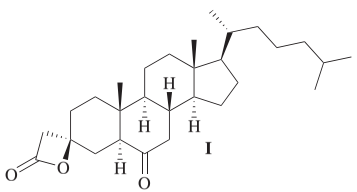
135



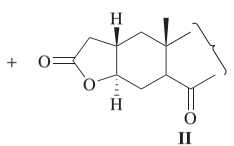
Cat.	I + II + III	I/II/III
2a	(89)	20:72:8
1a	(87)	62:6:32
4a	(86)	33:60:7
3a	(91)	70:4:26
8b	(86)	8:87:5
7c	(76)	66:16:20
5a	(85)	39:6:55
5d	(80)	44:7:49



Catalyst, DCM, reflux, 5.5 h

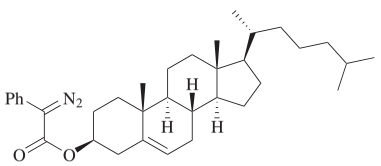
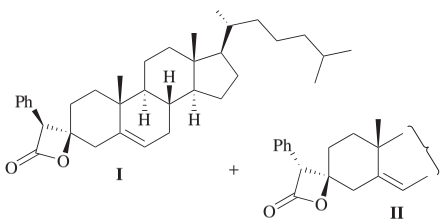


135



Cat.	I + II	I/II
2a	(85)	39:61
1a	(76)	92:8
4a	(88)	57:43
3a	(90)	97:3

TABLE 3. β-LACTONES FROM DIAZOACETATES (*Continued*)

Diazoacetate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{35} 	Catalyst, Solvent, reflux	 **I** + **II**	135

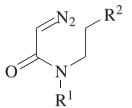
Cat.	Solvent	Time (h)	**I + II**	**I/II**
$Rh_2(OAc)_4$	DCM	2.5	(69)	22:78
6	DCM	5.5	(69)	16:84
5a	DCM	5.5	(66)	38:62
16b	DCM	5.5	(58)	16:84
16b	pentane	5.5	(69)	10:90

TABLE 4. γ-LACTAMS FROM DIAZOACETAMIDES

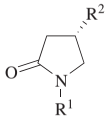
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables, not to the text discussion, for structures indicated by the **bold** numbers.*

$C_{6–8}$



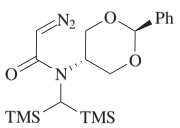
Catalyst, DCM, reflux, 6 h



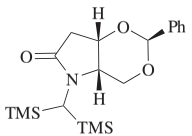
R^1	R^2	Cat.		% ee
$MeOCH_2CH_2$	MeO	**1a**	(72)	80
$MeOCH_2CH_2$	MeO	**3a**	(78)	77
t-Bu	EtO	**1a**	(95)	58
t-Bu	EtO	**3a**	(97)	78

138

C_6



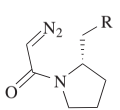
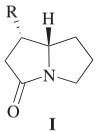
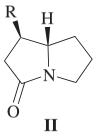
Catalyst, DCM



281, 282

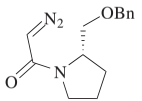
Cat.	Temp	Time (min)		% ee	
2a	rt	40	(72)	66	(4*S*,7*S*)
1a	rt	40	(82)	50	(4*R*,7*R*)
2a	reflux	20	(80)	44	(4*S*,7*S*)
1a	reflux	20	(84)	43	(4*R*,7*R*)
4a	rt	40	(72)	84	(4*R*,7*S*)
3a	rt	40	(76)	70	(4*R*,7*R*)
4a	reflux	20	(95)	90	(4*S*,7*S*)
3a	reflux	20	(92)	68	(4*R*,7*R*)
8b	reflux	180	(62)	1	—
7c	reflux	180	(88)	4	—
6	rt	20	(81)	78	(4*S*,7*S*)
5a	rt	20	(69)	66	(4*R*,7*R*)
6	reflux	20	(77)	77	(4*S*,7*S*)
5a	reflux	20	(80)	70	(4*R*,7*R*)
17d	reflux	180	(71)	29	(4*R*,7*R*)

TABLE 4. γ-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

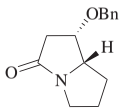
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 	Catalyst, DCM, reflux	 **I** +  **II**	283

R	Cat.	I + II	I/II
MeO	$Rh_2(OAc)_4$	(45)	53:47
MeO	**11**	(45)	63:37
MeO	**1a**	(95)	90:10
MeO	**2a**	(96)	73:27
MeO	**3a**	(99)	89:11
MeO	**7a**	(88)	97:3
MeO	**7c**	(97)	97:3
MeO	CuOTf	(55)	38:62
MeO	$CuPF_6$	(61)	36:64
MeO	**41b**	(83)	50:50
MeO	**42a**	(91)	47:53
Me	$Rh_2(OAc)_4$	(32)	18:82
Me	**11**	(20)	29:71
Me	**3a**	(98)	71:29
Me	**7a**	(86)	98:2
Me	**7c**	(95)	96:4
Me	CuOTf	(30)	20:80
Me	**41b**	(77)	29:71
Me	**42a**	(55)	35:65

C_7



Catalyst, DCM, reflux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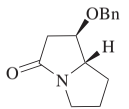
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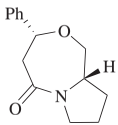
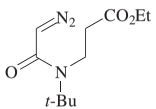


283

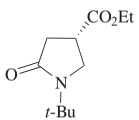
I **II** **III**

Cat.	**I + II + III**	**I/II/III**
$Rh_2(OAc)_4$	(41)	49:35:16
11	(20)	33:23:44
1a	(81)	90:9:1
2a	(87)	55:36:9
3a	(90)	89:11:0
7a	(94)	97:3:0
7c	(93)	96:4:0

C_9



Catalyst, DCM, reflux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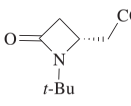
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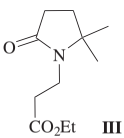
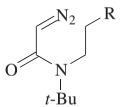
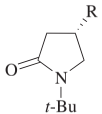
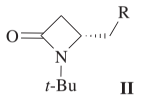


I **II** **III**

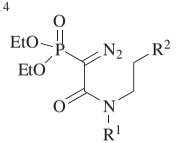
Cat.	Time (h)	**I + II + III**	**I/II/III**	% ee **I**	% ee **II**	
2a	10	(64)	2:9:89	—	44	138
3a	10	(54)	2:25:73	—	46	138
3c	10	(60)	12:88:<1	16	20	138
3b	8	(60)	16:82:2	8	43	274

TABLE 4. γ-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

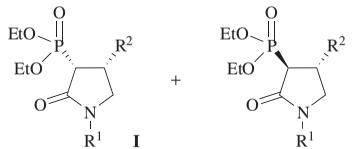
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11} 	Catalyst, DCM, reflux	 **I** +  **II**	

R	Cat.	Time (h)	I + II	I/II	% ee I	% ee II	
Et	**1a**	6	(74)	88:12	63	73	138
Et	**3a**	6	(82)	91:9	71	80	138
Et	**9**	6	(78)	90:10	64	71	138
Et	**3c**	10	(92)	92:8	<2	0	138
Et	**3b**	12.5	(78)	93:7	<4	40	274
i-Pr	**1a**	10	(91)	80:20	58	72	138
i-Pr	**3a**	10	(93)	82:18	69	65	138

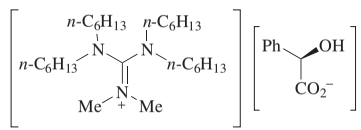
C_{10-14}



Catalyst, DCE

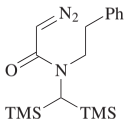
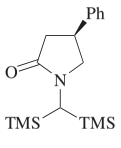
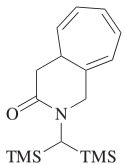


R^1	R^2	Cat.	Temp	Time (h)	**I** + **II**	**I**/**II**	% ee **II**	
n-Bu	Et	**3a**	reflux	24	(72)	0:100	14	334
n-Bu	Et	**16b**	reflux	4	(91)	14:86	7	334
n-Bu	Et	**16d**	reflux	4	(90)	14:86	1	334
n-Bu	Et	**17b**	reflux	4	(73)	17:83	12	334
n-Bu	Et	**24**	reflux	4	(87)	10:90	14	334
n-Bu	Et	**25**	reflux	4	(89)	15:85	10	334
t-Bu	Ph	**17b**	reflux	4	(70)	7:93	15	334
t-Bu	Ph	**24**	reflux	4	(76)	12:88	18	334
t-Bu	Ph	**24**	60°	24	(97)	11:89	22	334
t-Bu	Ph	**25**	reflux	4	(86)	17:83	40	334
t-Bu	Ph	**26**	reflux	4	(70)	7:93	21	334
t-Bu	Ph	**27**	reflux	4	(81)	7:93	16	334
t-Bu	Ph	**28**	reflux	4	(76)	6:94	24	334
t-Bu	Ph	$Rh_2(OAc)_4$	110°	3	(84)	33:67	27	335

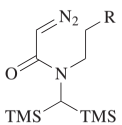
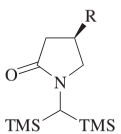


chiral ionic liquid used in the last entry of the sub-table

TABLE 4. γ-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

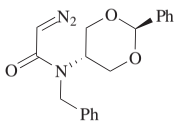
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	Catalyst, DCM, reflux	 +  **I** **II**	284

Cat.	I + II	I/II	% ee I	
2a	(87)	93:7	38	(*R*)
4a	(89)	95:5	43	(*R*)
6	(82)	96:4	34	(*R*)
8a	(86)	67:33	8	(*S*)
8b	(93)	78:22	0	—

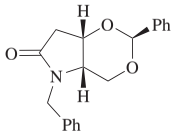
C_{12} 	Catalyst, DCM, reflux		284

R	Cat.		% ee	
4-$MeOC_6H_4$	**4a**	(83)	69	(*R*)
Bn	**2a**	(90)	32	(*R*)
Bn	**4a**	(92)	43	(*R*)

C_{12}

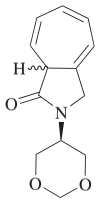


Catalyst, reflux, 2.5 h



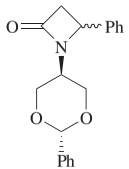
I

+



II

+

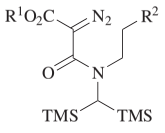
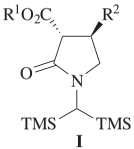
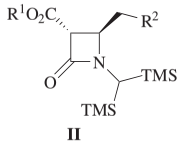


III

278

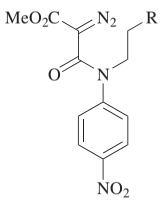
Cat.	Solvent	**I + II + III**	**I/II/III**	% ee **I**
$Rh_2(OAc)_4$	DCM	(22)	43:57:0	—
$Rh_2(OAc)_4$	DCE	(—)	54:46:0	—
1a	DCM	(75)	95:5:0	85
1a	DCE	(—)	67:33:0	—
3a	DCM	(61)	74:16:10	78
3a	DCE	(—)	69:21:10	—
5b	DCM	(45)	49:35:16	19
5b	DCE	(—)	25:47:28	—
7c	DCM	(48)	53:18:29	37
7c	DCE	(—)	42:50:8	—
16d	DCM	(9)	22:78:0	56
41b	DCM	(—)	44:47:9	—

TABLE 4. γ-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

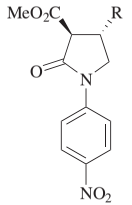
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-13} 	Catalyst	 **I** +  **II**	284

R^1	R^2	Cat.	Solvent	Temp	**I** + **II**	**I**/**II**	% ee **I**	
Me	Ph	**17b**	DCM	reflux	(92)	100:0	5	(3*R*,4*R*)
Me	Ph	**17c**	DCM	reflux	(87)	100:0	7	(3*R*,4*R*)
Me	Ph	**17d**	DCM	reflux	(80)	71:29	65	(3*R*,4*R*)
Me	Ph	**17d**	toluene	50°	(80)	50:50	75	(3*R*,4*R*)
Me	Ph	**16b**	DCM	reflux	(77)	100:0	9	—
Me	Ph	**5a**	DCM	reflux	(89)	100:0	35	(3*S*,4*S*)
Et	Ph	**17b**	DCM	reflux	(92)	100:0	—	—
Et	Ph	**17c**	DCM	reflux	(87)	100:0	—	—
Et	Ph	**17d**	DCM	reflux	(80)	55:45	—	—
Et	4-$MeOC_6H_4$	**17d**	DCM	reflux	(82)	90:10	51	(3*R*,4*R*)
Et	Bn	**17b**	DCM	reflux	(73)	100:0	24	—
Et	Bn	**17c**	DCM	reflux	(90)	85:15	44	—
Et	Bn	**17d**	DCM	reflux	(75)	56:44	64	—

C_{12-17}



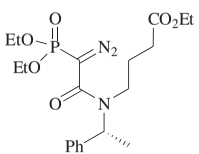
Catalyst



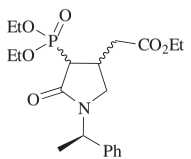
250

R	Cat.	Solvent	Temp (°)	Time (h)		% ee	
Me	**17d**	DCM	20	3	(82)	33	(3*S*,4*S*)
Et	**17d**	DCM	20	4	(84)	34	(3*S*,4*S*)
Ph	**17b**	DCM	20	4	(82)	47	(3*S*,4*R*)
Ph	**17b**	Et_2O	20	4	(—)	45	(3*S*,4*R*)
Ph	**17b**	toluene	20	4	(—)	37	(3*S*,4*R*)
Ph	**17a**	DCM	20	5	(83)	47	(3*S*,4*R*)
Ph	**17c**	DCM	20	3	(82)	26	(3*S*,4*R*)
Ph	**17d**	DCM	20	5	(80)	73	(3*S*,4*R*)
Ph	**16d**	DCM	20	4	(87)	6	(3*S*,4*R*)
4-ClC_6H_4	**17d**	DCM	23	6	(83)	82	(3*S*,4*R*)
4-$O_2NC_6H_4$	**17d**	DCM	20	8	(81)	73	(3*S*,4*R*)
4-$MeOC_6H_4$	**17d**	DCM	20	4	(72)	81	(3*S*,4*R*)

C_{14}



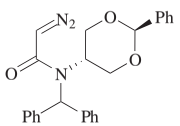
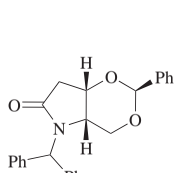
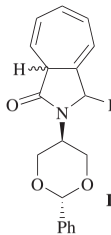
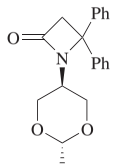
Catalyst **24**, DCE, reflux, 4 h



(40) dr 1.7:1

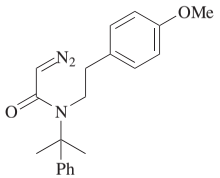
334

TABLE 4. γ-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

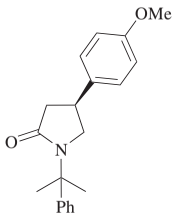
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}  *y* M	Catalyst (*x* mol %), Solvent, reflux	 **I** +  **II** +  **III**	281, 282

y	Cat.	*x*	Solvent	Time (min)	**I** + **II** + **III**	**I**/**II**/**III**	% ee **I**	% ee **II**
0.009	**2a**	10	DCM	5	(98)	1:96:3	—	3
0.009	**1a**	10	DCM	5	(52)	35:35:30	94	28
0.009	**2a**	1	DCM	5	(81)	10:81:9	88	50
0.009	**1a**	1	DCM	5	(52)	34:38:28	95	22
0.009	**2a**	0.1	DCM	60	(87)	12:78:10	78	32
0.009	**1a**	0.1	DCM	60	(66)	18:50:32	>95	33
0.27	**2a**	0.1	DCM	60	(75)	9:75:16	81	34
0.009	**1a**	0.1	DCE	60	(74)	19:66:15	75	7
0.009	**4a**	1	DCM	5	(48)	35:23:42	86	62
0.009	**3a**	1	DCM	5	(61)	32:35:33	87	38
0.009	**4a**	0.1	DCM	60	(55)	18:47:35	82	13
0.009	**8b**	1	DCM	5	(85)	10:69:21	29	20
0.009	**7c**	1	DCM	5	(82)	8:55:37	64	5

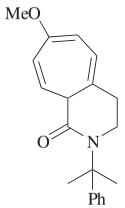
C_{19}



Catalyst, Solvent



+



275

I **II**

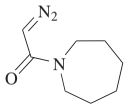
Cat.	Solvent	Temp	Time (h)	**I + II**	**I/II**	% ee **I**	
16b	DCM	reflux	1.5	(36)	47:53	3	(*R*)
20a	DCM	reflux	1.5	(25)	58:42	2	(*R*)
20b	DCM	reflux	1.5	(36)	53:47	13	(*R*)
1a	DCM	reflux	1.5	(53)	87:13	18	(*S*)
3a	DCM	reflux	1.5	(72)	>98:2	47	(*S*)
3a	DCM	20°	—	(76)	>98:2	52	(*S*)
3a	DCM	0°	—	(69)	>98:2	52	(*S*)
3a	DCE	20°	—	(74)	>98:2	37	(*S*)
3a	toluene	20°	—	(71)	>98:2	47	(*S*)
3a	THF	40°	—	(69)	>98:2	41	(*S*)
3a	Et_2O	reflux	—	(73)	>98:2	46	(*S*)
3a	dioxane	40°	—	(70)	>98:2	54	(*S*)

TABLE 5. β-LACTAMS FROM DIAZOACETAMIDES

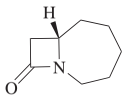
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables, not to the text discussion, for structures indicated by the **bold** numbers.*

C_8

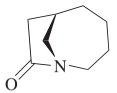


Catalyst, DCM, reflux



I

+

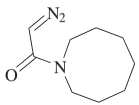


II

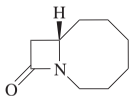
277

Cat.	I + II	I/II	% ee I
1a	(67)	100:0	97
3a	(68)	99:1	92
7a	(—)	—	<50

C_9

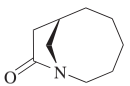


Catalyst, Solvent, reflux



I

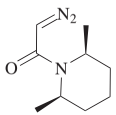
+



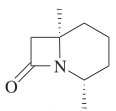
II

277

Cat.	Solvent	I + II	I/II	% ee I	% ee II
1a	DCM	(77)	40:60	31	97
1a	DCE	(67)	67:33	30	96
3a	DCM	(95)	26:74	15	98
3a	DCE	(68)	49:51	8	96
7a	DCE	(81)	39:61	66	96

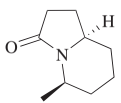


Catalyst, DCM, reflux



I

+

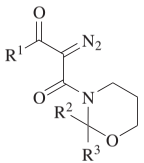


II

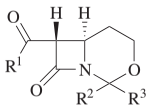
277

Cat.	I + II	I/II	% ee I
1a	(78)	89:11	86
3a	(—)	85:15	86
7a	(—)	86:14	4

C_{9-11}



Catalyst, DCM



R^1	R^2	R^3	Cat.	Temp (°)	Time (h)		% ee
MeO	Me	Me	**17a**	0	6	(89)	93
Me	Me	Me	**17b**	rt	6	(84)	0
MeO	Et	Et	**17a**	0	8	(89)	83

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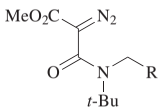
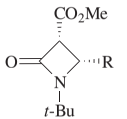
C_{10-14}



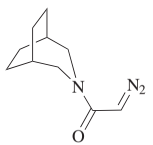
Catalyst **17b**, DCM



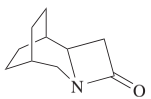
R	Temp (°)	Time (h)		% ee	
MeO_2CCH_2	22	8	(98)	56	(3*R*,4*S*)
n-Pr	16	5	(97)	60	(3*R*,4*S*)
Ph	22	6	(94)	74	(3*R*,4*R*)

249

C_{10}



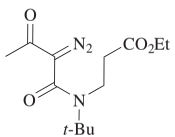
Catalyst, DCM, reflux



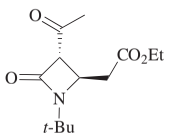
Cat.		% ee
1a	(70)	96
3a	(80)	93
7a	(—)	<50

277

C_{11}



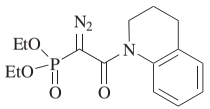
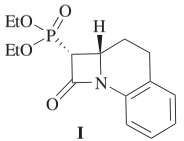
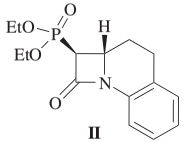
Catalyst **38**, DCM, rt, 8 h



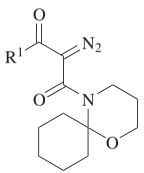
(93) 26% ee

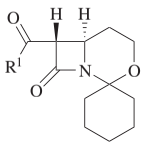
64

TABLE 5. β-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	Catalyst, DCE, reflux, 4 h	 **I** +  **II**	334

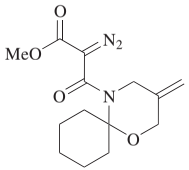
Cat.	I + II	I/II	% ee II
$Rh_2(OAc)_4$	(73)	21:79	—
17b	(80)	25:75	10
24	(65)	25:75	2
25	(75)	17:83	5
26	(65)	28:72	16
27	(73)	7:93	15
28	(67)	22:78	6

C_{13} 

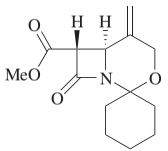
Catalyst, DCM 

R^1	Cat.	Temp	Time (h)		% ee		Refs.
MeO	**17a**	0°	2	(94)	96	(6'*R*,7'*R*)	333
MeO	**17b**	0°	3	(89)	90	(6'*R*,7'*R*)	333
MeO	**17c**	0°	3	(86)	92	(6'*R*,7'*R*)	333
MeO	**17d**	0°	4	(85)	93	(6'*R*,7'*R*)	333
MeO	**17e**	0°	3	(85)	92	(6'*R*,7'*R*)	333
MeO	**22**	rt	24	(58)	50	(6'*R*,7'*R*)	287
MeO	**23a**	rt	36	(62)	52	(6'*R*,7'*R*)	287
MeO	**23b**	rt	18	(71)	52	(6'*R*,7'*R*)	287
Me	**17b**	rt	6	(84)	0	—	333

C_{13}

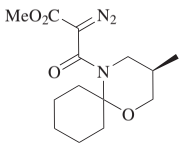


Catalyst **17a**, DCM, rt, 13 h

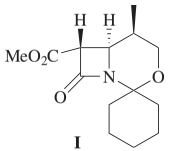


(83) 88% ee

333

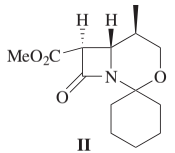


Catalyst, DCM, rt



I

+

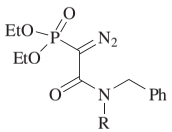
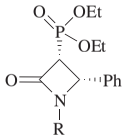
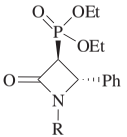


II

Cat.	Time (h)	**I + II**	**I/II**
$Rh_2(OAc)_4$	18	(75)	25:75
18a	18	(77)	2:98
17b	24	(47)	85:15

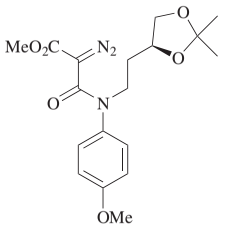
288

TABLE 5. β-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

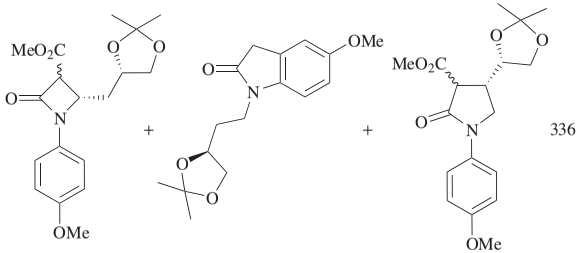
Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{13–16}$ 	Catalyst, DCE	 +  **I** **II**	334

R	Cat.	Temp	Time (h)	**I** + **II**	**I**/**II**	% ee **II**
t-Bu	**17b**	reflux	4	(83)	83:17	20
t-Bu	**24**	reflux	4	(81)	70:30	11
t-Bu	**24**	60°	48	(91)	80:20	16
t-Bu	**25**	reflux	4	(90)	80:20	15
t-Bu	**26**	reflux	4	(76)	91:9	15
t-Bu	**27**	reflux	4	(94)	82:18	6
t-Bu	**28**	reflux	4	(88)	94:6	15
Bn	**3a**	reflux	48	(52)	29:71	1
Bn	**16b**	reflux	4	(80)	20:80	10
Bn	**16d**	reflux	4	(65)	20:80	8
Bn	**17b**	reflux	4	(72)	17:83	28
Bn	**24**	reflux	4	(60)	19:81	26
Bn	**25**	reflux	4	(70)	25:75	40

C_{13}



Catalyst, Solvent

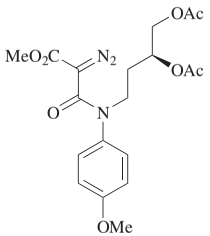
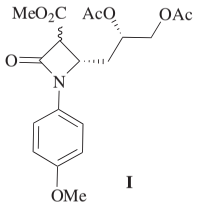
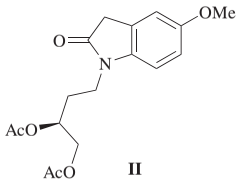


I **II** **III**

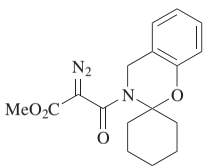
336

Cat.	Solvent	Temp (°)	**I + II + III**	**I/II/III**
$Rh_2(OAc)_4$	DCM	30	(75)	50:0:50
$Rh_2(OAc)_4$	DCM	45	(64)	60:0:40
$Rh_2(OAc)_4$	benzene	rt	(82)	55:0:45
$Rh_2(OAc)_4$	benzene	80	(60)	71:0:29
$Rh_2(OOct)_4$	DCM	rt	(65)	63:0:37
$Rh_2(OPiv)_4$	benzene	80	(56)	83:0:17
17b	DCM	30	(47)	40:60:0
$Rh_2(acam)_4$	benzene	80	(17)	0:100:0

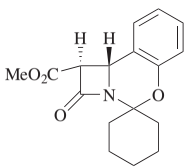
TABLE 5. β-LACTAMS FROM DIAZOACETAMIDES (*Continued*)

Diazoacetamide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	Catalyst **17b**, DCE	 **I** +  **II**	336

Temp (°)	I + II	I/II
30	(77)	71:29
60	(78)	57:43

C_{16} 

Catalyst, Solvent



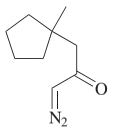
Cat.	Solvent	Temp (°)	Time (d)		% ee	
17a	DCM	rt	5	(62)	41	
17a	toluene	rt	3	(60)	70	
17a	toluene	0	4	(71)	84	285
17b	toluene	0	4	(51)	83	
17c	toluene	0	4	(56)	45	
17e	toluene	0	3	(78)	10	
17d	toluene	0	4	(66)	84	

TABLE 6. SYNTHESIS OF CYCLOALKANE DERIVATIVES

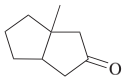
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables, not to the text discussion, for structures indicated by the **bold** numbers.*

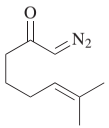
C_9



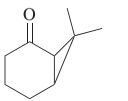
Catalyst, CH_2Cl_2, rt



Cat.		% ee	
$Rh_2(OAc)_4$	(80)	—	
1a	(58)	0	155
3c	(78)	0	
3b	(58)	7	



Catalyst, Solvent, reflux



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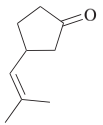


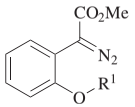
I **II**

Cat.	Solvent	**I** + **II**	**I**/**II**	% ee **I**	% ee **II**	
39a	pentane	(99)	91:9	55	83	68
39a	DCM	(99)	50:50	20	80	68
39b	pentane	(87)	93:7	80	91	68
39b	DCM	(74)	67:33	63	93	68
39c	pentane	(92)	69:31	80	94	68
39c	DCM	(93)	51:49	63	92	68
1a	DCM	(67)	76:24	17	1	291
7c	DCM	(75)	71:29	8	8	291

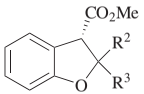
TABLE 6. SYNTHESIS OF CYCLOALKANE DERIVATIVES (*Continued*)

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

C_{9-11}

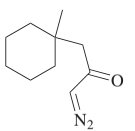


Catalyst, Solvent

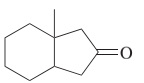


R^1	R^2	R^3	Cat.	Solvent	Temp (°)	Time (h)		% ee	
Me	H	H	**16b**	hexanes	−50	72	(98)	<5	307
Me	H	H	**21a**	DCM	−50	72	(70)	43	307
Me	H	H	**21b**	DCM	−50	72	(70)	68	307
Me	H	H	**17d**	toluene	−23	1	(69)	44	218
i-Pr	Me	Me	**17d**	toluene	−78	1.5	(88)	22	218
i-Pr	Me	Me	**16b**	hexanes	−50	72	(98)	94	307
i-Pr	Me	Me	**21a**	DCM	−50	72	(48)	60	307
i-Pr	Me	Me	**21b**	DCM	−50	72	(57)	65	307

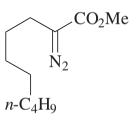
C_{10}



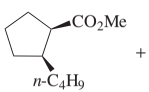
Catalyst, DCM, rt



Cat.		% ee	Refs.
$Rh_2(OAc)_4$	(77)	—	155
1a	(33)	0	



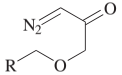
Catalyst **17d**, toluene, −78°, 1.5 h



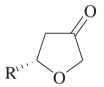
I + **II** (90) **I/II** = 10:90, 94% ee **II** 309

I **II**

C_{10-11}



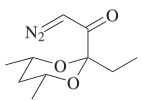
Catalyst, Solvent, 6 h



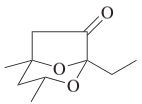
(*R*) 337

R	Cat.	Solvent	Temp		% ee
c-C_6H_{11}	**34**	pentane	–78°	(52)	67
n-C_7H_{15}	**16b**	DCM	rt	(28)	13
n-C_7H_{15}	**16d**	DCM	rt	(31)	14
n-C_7H_{15}	**1a**	DCM	reflux	(84)	8
n-C_7H_{15}	**34**	DCM	rt	(80)	37
n-C_7H_{15}	**34**	pentane/DCM (10:1)	–78°	(87)	36
n-C_7H_{15}	**34**	PhF	–40°	(65)	30
n-C_7H_{15}	**34**	pentane	rt	(79)	33
n-C_7H_{15}	**34**	pentane	–45°	(72)	71

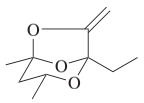
C_{10}



Catalyst, DCM, reflux



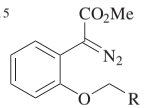
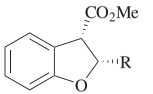
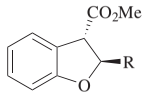
+



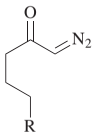
I **II** 292

Cat.	**I**	% ee **I**	**II**	% ee **II**
$Rh_2(OAc)_4$	(58)	—	(28)	—
17b	(36)	20	(10)	10
16b	(31)	7	(0)	—
16d	(17)	<5	(5)	<5
1a	(11)	<5	(8)	7

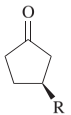
TABLE 6. SYNTHESIS OF CYCLOALKANE DERIVATIVES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)								Refs.
$C_{10–15}$ 	Catalyst, Solvent	 **I** +  **II**								
	R	Cat.	Solvent	Temp (°)	Time (h)	**I** + **II**	**I**/**II**	% ee **I**	% ee **II**	
	Me	**16b**	hexanes	−50	72	(85)	80:20	60	—	307
	Me	**21a**	DCM	−50	72	(50)	85:15	53	—	307
	Me	**21b**	DCM	−50	72	(70)	88:12	45	—	307
	Me	**17d**	toluene	−78	0.5	(91)	14:86	78	97	218
	vinyl	**17d**	toluene	−23	2	(62)	77:23	86	92	218
	c-C_6H_{11}	**16b**	hexanes	−50	72	(72)	95:5	63	—	307
	c-C_6H_{11}	**21a**	DCM	−50	72	(22)	60:40	22	—	307
	c-C_6H_{11}	**21b**	DCM	−50	72	(35)	75:25	35	—	307
	c-C_6H_{11}	**17d**	toluene	−78	7	(63)	96:4	96	—	218
	Ph	**16b**	hexanes	rt	0.5	(60)	60:40	38	—	338
	Ph	**17f**	hexanes	rt	0.5	(83)	>30:1	87	—	338
	Ph	**18b**	hexanes	−60	—	(79)	>30:1	95	—	338
	Ph	**35a**	toluene	rt	5	(68)	95:5	78	—	306
	Ph	**17b**	toluene	−60	0.5	(86)	70:30	70	80	218
	Ph	**17a**	toluene	−60	0.5	(84)	81:19	61	79	218
	Ph	**17c**	toluene	−60	0.5	(86)	89:11	61	69	218
	Ph	**17e**	toluene	−60	0.5	(83)	99:1	71	—	218
	Ph	**17d**	toluene	−60	0.5	(87)	100:0	90	—	218
	Ph	**19b**	toluene	−60	1	(57)	68:32	65	77	218
	Ph	**19a**	toluene	−60	1	(69)	82:18	63	80	218
	Ph	**19c**	toluene	−60	0.5	(73)	89:11	61	57	218
	Ph	**19d**	toluene	−60	0.5	(84)	100:0	86	—	218
	Ph	**17d**	DCM	−45	0.5	(63)	100:0	90	—	218
	Ph	**17d**	Et_2O	−10	0.5	(78)	100:0	88	—	218
	Ph	**17d**	hexanes	rt	0.2	(78)	100:0	70	—	218
	Ph	**17d**	toluene	−78	1	(86)	100:0	94	—	218
	Ph	**19d**	toluene	−78	12	(70)	100:0	91	—	218
	3,4-$(TBSO)_2C_6H_3$	**17d**	toluene	−78	2	(85)	99:1	91	—	218

C_{11}



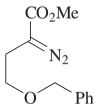
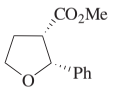
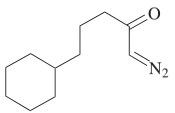
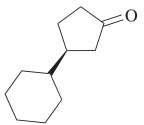
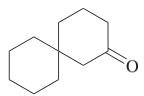
Catalyst, DCM, reflux



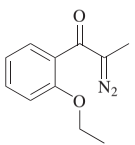
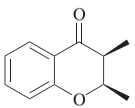
254

R	Cat.	Time (h)		% ee	
Ph	**39a**	1	(80)	45	(*S*)
Ph	**39b**	1	(73)	54	(*S*)
Ph	**39c**	1	(78)	40	(*S*)
Ph	**39d**	48	(65)	17	(*S*)
Ph	**39e**	48	(68)	48	(*S*)
Ph	**39f**	1	(64)	32	(*S*)
Ph	**39g**	1	(68)	51	(*R*)
Ph	**39h**	1	(0)	—	—
Ph	**40**	1	(0)	—	—
Ph	**16f**	1	(0)	—	—
4-FC_6H_4	**39a**	1	(68)	60	(*S*)
4-FC_6H_4	**39b**	1	(61)	58	(*S*)
4-FC_6H_4	**39d**	48	(44)	40	(*S*)
4-FC_6H_4	**39e**	48	(18)	60	(*S*)
4-FC_6H_4	**39f**	1	(61)	36	(*S*)
4-FC_6H_4	**39g**	1	(70)	36	(*R*)
4-ClC_6H_4	**39a**	1	(87)	65	(*S*)
4-ClC_6H_4	**39b**	1	(74)	59	(*S*)
4-ClC_6H_4	**39c**	1	(87)	73	(*S*)
4-ClC_6H_4	**39d**	48	(63)	57	(*S*)
4-ClC_6H_4	**39e**	48	(0)	—	—
4-ClC_6H_4	**39f**	1	(54)	46	(*S*)
4-ClC_6H_4	**39g**	1	(54)	33	(*R*)
4-$MeOC_6H_4$	**39a**	1	(86)	22	(*S*)
4-$MeOC_6H_4$	**39b**	1	(75)	7	(*S*)
4-$MeOC_6H_4$	**39c**	1	(74)	28	(*S*)
4-$MeOC_6H_4$	**39d**	48	(87)	3	(*S*)
4-$MeOC_6H_4$	**39e**	48	(78)	30	(*S*)
4-$MeOC_6H_4$	**39f**	1	(78)	36	(*S*)
4-$MeOC_6H_4$	**39g**	1	(95)	56	(*R*)

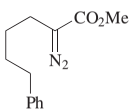
TABLE 6. SYNTHESIS OF CYCLOALKANE DERIVATIVES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	Catalyst **17d**, toluene, –78°, 1 h	 (91) 41% ee	218
	Catalyst, DCM, reflux	 + 	254

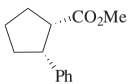
	I		II		
Cat.	Time (h)	I + II	I/II	% ee I	I
39a	1	(71)	56:44	66	(*S*)
39b	1	(74)	41:59	74	(*S*)
39c	1	(82)	45:55	47	(*S*)
39d	48	(54)	46:54	44	(*S*)
39e	48	(73)	41:59	57	(*S*)
39f	1	(0)	—	—	—
39g	1	(99)	81:19	9	(*R*)
40	1	(0)	—	—	—
16f	1	(99)	84:16	8	(*R*)

	Catalyst **16c**, DCM, reflux, 14 h	 (89) 82% ee	180

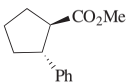
C_{12}



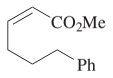
Catalyst



I



II



III

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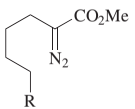
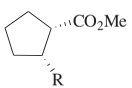
Cat.	Solvent	Temp (°)	Time (h)	I + II + III	I/II/III	% ee I	% ee II
17d	toluene	−78	0.5	(85)	100:0:0	95	—
17d	toluene	−45	0.2	(85)	91:0:9	90	—
17d	toluene	0	0.1	(80)	82:0:18	81	—
17d	DCM	−78	0.5	(76)	93:0:7	95	—
17d	Et_2O	−78	0.5	(73)	97:0:3	94	—
17b	toluene	−78	7	(73)	56:37:7	89	27
17a	toluene	−78	30	(69)	73:19:8	90	56
17c	toluene	−78	6	(80)	77:20:3	95	22
19d	toluene	−78	0.5	(76)	100:0:0	67	—
17d	toluene	−78	9	(82)	100:0:0	95	—

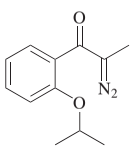


Catalyst **17d**, toluene, −78°, 0.5 h

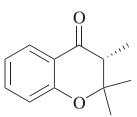


R		% ee
4-ClC_6H_4	(81)	93
4-$MeOC_6H_4$	(85)	92

309



Catalyst, DCM, reflux, 12 h

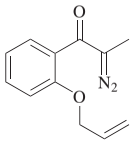
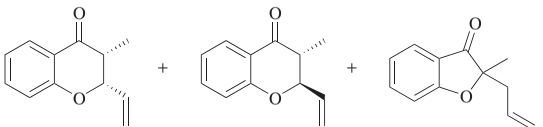


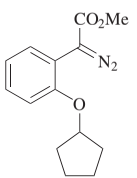
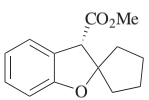
(100)

Cat.	% ee
$Rh_2(OAc)_4$	—
16c	50
16e	23
16g	18
32	30
24	10

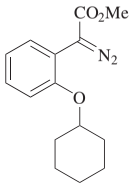
180

TABLE 6. SYNTHESIS OF CYCLOALKANE DERIVATIVES (*Continued*)

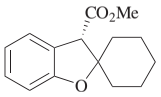
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	Catalyst, DCM, 12 h	 **I** + **II** + **III**	

Cat.	Temp	**I** + **II**	**I/II**	% ee **I**	% ee **II**	**III**	
$Rh_2(OAc)_2$	reflux	(97)	74:26	—	—	(3)	180
16c	reflux	(97)	93:7	60	—	(3)	180
16c	0°	(—)	—	79	—	(—)	180
16e	reflux	(96)	85:15	31	18	(4)	180
16g	reflux	(96)	83:17	10	7	(4)	180
31	reflux	(82)	75:25	20	—	(18)	180
32	reflux	(97)	92:8	40	—	(3)	180
33	reflux	(90)	92:8	8	—	(10)	180
24	reflux	(88)	86:14	20	11	(12)	180
1a	reflux	(96)	74:26	0	0	(4)	180
$Cu(acac)_2$	reflux	(0)	—	—	—	(100)	180
43	reflux	(0)	—	—	—	(100)	180
41a	reflux	(0)	—	—	—	(100)	180
C_{13} 	Catalyst **16b**, hexanes, –50°, 72h	 (93) 90% ee	307

C_{14}

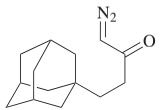


Catalyst **16b**, hexanes, –50°, 72 h

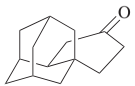


(12) 80% ee

307



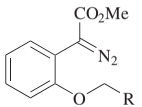
Catalyst **3a**, DCM, rt



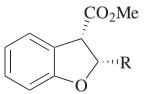
(64) 70% ee

183

$C_{15–16}$

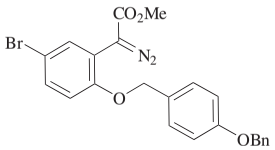
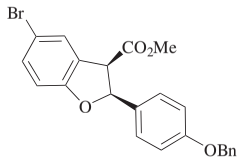
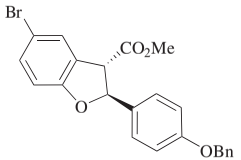
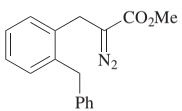
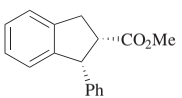
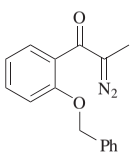
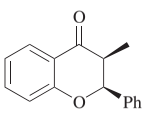
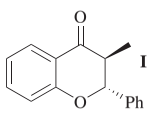


Catalyst **17d**, toluene, –78°



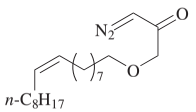
R	Time (h)		% ee		
4-ClC_6H_4	1.5	(79)	94	—	218
4-$MeOC_6H_4$	1	(89)	94	(2*R*,3*S*)	
4-MeC_6H_4	1.5	(84)	91	—	

TABLE 6. SYNTHESIS OF CYCLOALKANE DERIVATIVES (*Continued*)

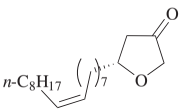
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	Catalyst, DCM, 0.5 h	 +  **I** **II**	338
C_{16}			
	Catalyst **17d**, toluene, −78°, 1.5 h	 (85) 92% ee	309
	Catalyst **16c**, DCM, reflux, 12 h	 +  **I** **II**	**I** + **II** (100) **I/II** = 80:20, 62% ee **I**	180, 294

Cat.	Temp	**I** + **II**	**I/II**	% ee **I**	% ee **II**
16b	rt	(72)	2:3	—	32
17d	rt	(79)	13:1	57	—
17d	0°	(71)	14:1	65	—
17f	rt	(83)	14:1	65	—
17f	0°	(72)	14:1	79	—
18b	0°	(49)	14:1	79	—

C_{21}

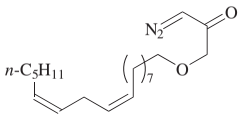


Catalyst, Solvent, 6 h

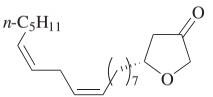


(*R*)

Cat.	Solvent	Temp (°)		% ee	
16b	DCM	0	(31)	23	
17b	DCM	0	(67)	16	337
34	pentane	0	(60)	47	
34	pentane	−78	(62)	83	



Catalyst **34**, pentane, −78°, 6 h



(52) 67% ee, (*R*) 337

[a] The results shown are the average of 3 trials.

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CHAPTER 2

CYCLOADDITIONS OF CARBONYL YLIDES DERIVED FROM DIAZOCARBONYL COMPOUNDS

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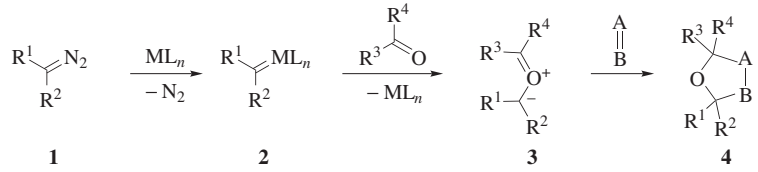
INTRODUCTION

Metal-catalyzed decomposition of diazo compounds **1** lead to transient metallocarbenes **2**, which can generate carbonyl ylide intermediates **3** by interaction with carbonyl systems. The carbonyl ylide intermediates **3** subsequently undergo cycloaddition if suitable dipolarophiles (A=B) are present (Scheme 1). Such a catalyzed cascade process can rapidly generate molecular complexity associated with the creation of 5-membered oxacycles **4** from readily available starting materials, and thus constitutes a useful transformation in organic synthesis.[1–26] This chapter covers the metal-catalyzed intra- and intermolecular cycloadditions of carbonyl ylides derived from diazocarbonyl compounds with various dipolarophiles. The literature up to the end of 2011 is covered.

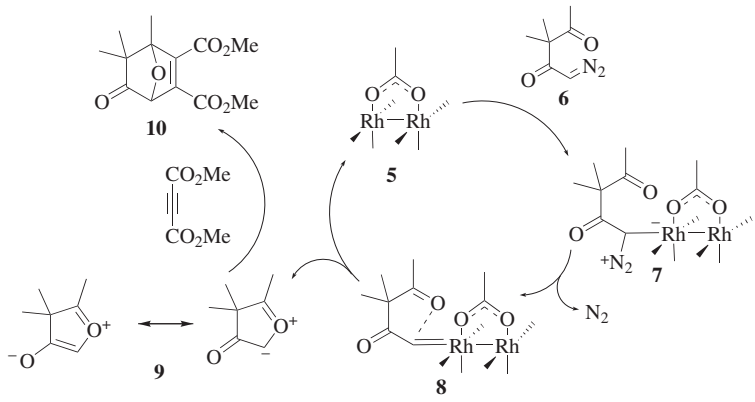


Scheme 1

MECHANISM AND STEREOCHEMISTRY

Despite the synthetic utility of diazocarbonyl compounds for the generation of carbonyl ylide intermediates, definitive mechanistic studies on the metal-catalyzed formation and cycloaddition of carbonyl ylides are lacking. Because of the high catalytic turnover frequencies in these reactions, structural information about the intermediates is difficult to obtain. However, some advances have been made that impact the mechanistic understanding of these transformations. Stable ruthenium-carbenoid complexes[27–29] and one rhodium metallocarbene[30] have been characterized by X-ray crystallography. As these systems are also capable of inducing catalytic carbenoid transformations, the X-ray crystallographic data provide supporting evidence for putative metallocarbene intermediates in catalytic reactions. Computational methods have also been used to determine the structure of carbenoid intermediates.[31–33] A typical carbonyl ylide reaction is generally accepted as proceeding roughly as shown in Scheme 2 for a cyclic carbonyl ylide with dimethyl acetylenedicarboxylate (DMAD).

Reaction of diazo compound **6** with catalyst **5** forms diazonium complex **7**, which then extrudes nitrogen to generate metallocarbene **8** in the rate-limiting step.[34,35] Interaction of **8** with a carbonyl group, intramolecularly in the example shown in Scheme 2, forms a carbonyl ylide **9**, possibly reversibly (see Eqs. 1 and 2 and associated discussion). Carbonyl ylide **9** subsequently undergoes cycloaddition with DMAD to generate cycloadduct **10**. Although not shown in Scheme 2 for the sake of clarity, the metal catalyst may, at least in some cases, remain associated with the ylide during the ensuing cycloaddition.[36] Whether or not the latter process occurs has important implications for the possibility of



Scheme 2

the catalyst to influence the selectivity of the cycloaddition, especially enantioselectivity using a chiral catalyst with achiral substrates. Energy is necessary to effect catalyst dissociation,[37] and part of this energy could be supplied in bond formation to the dipolarophile. Cycloaddition would then occur on the face of the ylide opposite to that of the catalyst as the metal dissociates. Computational studies indicate that in a metal-carbene complex such as **8** the Rh−C σ-bond and the adjacent C=O π-bonds tend towards alignment, and thus have partial metal enolate-type interactions.[38–41] This latter work suggests that a transition structure for cyclization to form a metal-complexed ylide might resemble the structure illustrated in Fig. 1, shown as derived from a 2-diazo-1,3,6-tricarbonyl substrate.

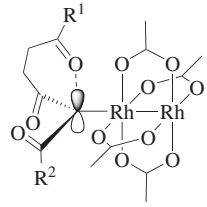
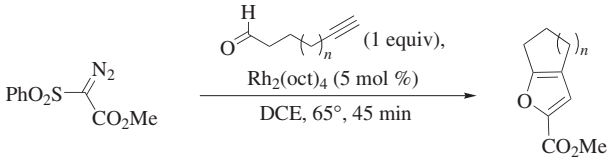


Figure 1. Possible transition state for formation of a metal-complexed cyclic ylide.

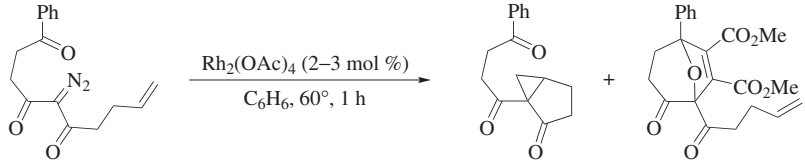
Experimental support for reversible ylide formation is found for reaction of a diazosulfone with two unsaturated aldehydes that compete for the diazosulfone in intermolecular carbonyl ylide formation–intramolecular cycloaddition.[42] When used separately, 5-hexynal and 6-heptynal both undergo cycloaddition followed by elimination of benzenesulfinic acid, leading to a furan fused to either a five- or six-membered ring, respectively (Eq. 1). In the competition experiment only the furan from 6-heptynal is observed. Since both aldehydes are expected to form carbonyl ylides at similar rates then, at least for 5-hexynal, aldehyde regeneration from the ylide must occur.



n	Yield (%)
1	46
2	65

(Eq. 1)

The following set of results also suggest the reversibility of carbonyl ylide formation.[43] An unsaturated diazotrione fails to undergo intramolecular cyclization–cycloaddition under Rh(II) catalysis and cyclopropanation is the only observed reaction pathway (Eq. 2). The isolation of a product derived from cyclopropanation suggests that carbonyl ylide formation might be disfavored in this instance. To investigate this hypothesis, the experiment was repeated in the presence of DMAD, which gives the cycloadduct derived from intermolecular carbonyl ylide cycloaddition as the major product (cycloadduct/cyclopropane 82:18). This study suggests that a catalyst-complexed carbonyl ylide forms in both cases, but is unable to undergo cycloaddition to the tethered alkene, possibly because the carbonyl group in the tether results in the parallel-plane orientation approach required for cycloaddition not being easily achievable. In the absence of DMAD, this intermediate might revert to the rhodium metallocarbene, which then undergoes intramolecular cyclopropanation. It is also possible that cycloaddition and cyclopropanation proceed by way of a common intermediate, which is not necessarily formed reversibly. Because variation of the catalyst has no effect on the cycloadduct to cyclopropane ratio, this intermediate is most straightforwardly assigned as the catalyst-free carbonyl ylide.



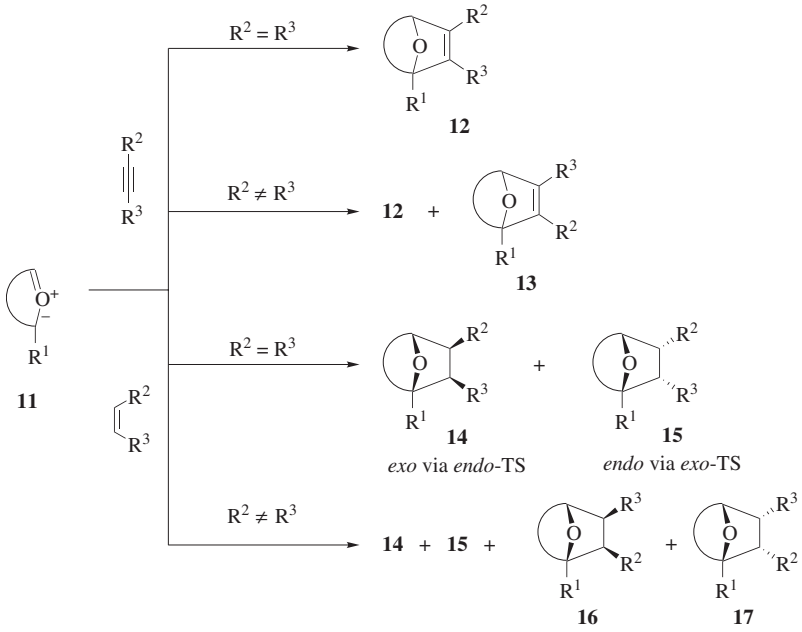
Additive		
—	81	—
DMAD (1.1 equiv)	15	68

(Eq. 2)

Regioselectivity

Cycloaddition regioselectivity is not an issue for symmetrically substituted alkynyl and alkenyl dipolarophiles. With unsymmetrical dipolarophiles, which are not constrained to one orientation for cycloaddition by tethering to the ylide **11**, regioselectivity can be a complicating issue as shown by the potential array of cycloaddition products with an alkyne (**12** and **13**) and an alkene (**14**–**17**) (Scheme 3). Nonetheless, one constitutional isomer often predominates, especially with highly unsymmetrical dipolarophiles.

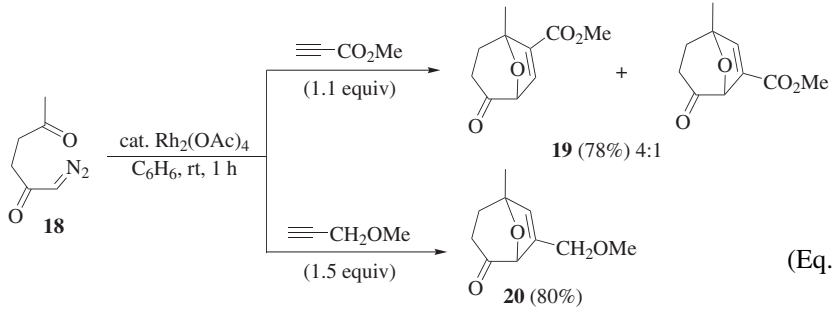
Although the potential influence of steric effects on regioselectivity cannot be ignored, carbonyl ylide cycloaddition regioselectivity has generally been rationalized by application of frontier molecular orbital (FMO) theory,[44–49] and more



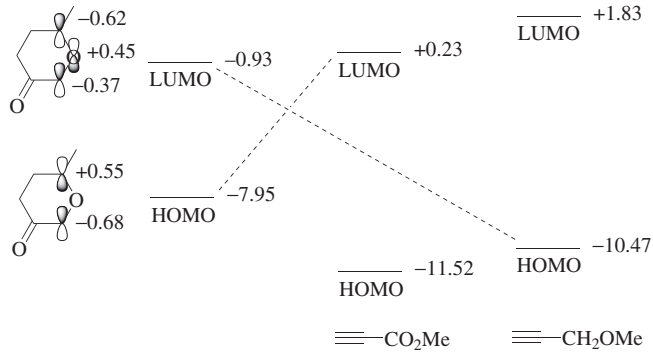
Scheme 3

recently density functional theory (DFT).[50] According to FMO theory, the preferred constitutional isomer will be that in which the atoms bearing the larger coefficients of the dominant interacting frontier orbitals overlap. Of the three categories originally described by Sustmann,[51] type II is particularly common for carbonyl ylides since they possess one of the smallest LUMO–HOMO gaps of the common 1,3-dipo1es.[52,53] That is, both $LUMO_{dipolarophile}-HOMO_{dipole}$ and $LUMO_{dipole}-HOMO_{dipolarophile}$ separations must often be taken into account. Two examples where the experimentally observed outcomes have been computationally rationalized are cycloadditions of the carbonyl ylide derived from the diazodione **18** with methyl propiolate and with methyl propargyl ether.[7,45] In benzene, $Rh_2(OAc)_4$-catalyzed reaction of diazodione **18** with methyl propiolate or methyl propargyl ether results in a 4:1 mixture of cycloadducts **19**, and exclusively cycloadduct **20**, respectively (Eq. 3).[45] The strongest FMO interaction for methyl propiolate is between its LUMO, where the terminal carbon of the alkyne possesses the largest coefficient, and the HOMO of the carbonyl ylide where the largest coefficient is on the carbon proximal to the keto group, representing a dominant type I ($LUMO_{dipolarophile}$-$HOMO_{dipole}$) interaction (Scheme 4). For the more electron-rich methyl propargyl ether, the energy difference between type I ($\Delta E = 9.78$ eV) and type III ($LUMO_{dipole}$-$HOMO_{dipolarophile}$, $\Delta E = 9.54$ eV) interactions is relatively small. This cycloaddition can be considered a type II case where the regioselectivity is influenced most by the larger relative difference in the terminal coefficient sizes in the LUMO of the dipole. In this case

the largest coefficient is on the carbon distal to the keto group, which interacts with the HOMO of methyl propargyl ether (where the larger coefficient is on the terminal carbon).

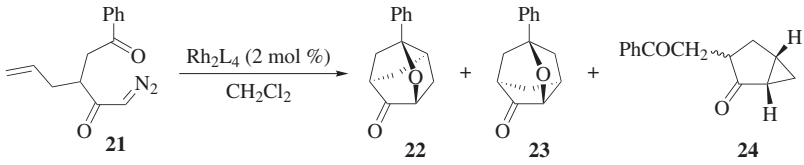


(Eq. 3)



Scheme 4

A simplistic FMO analysis is complicated by the possibility that the catalyst used to form the carbonyl ylide may interact with the ylide at the time of the cycloaddition. For example in Eq. 4, while tethering of the dipolarophile at a position within a cyclic ylide necessarily results in the intramolecular cycloaddition being *endo* selective, the regioselectivity observed shows catalyst dependency. The major constitutional isomer formed from diazocarbonyl substrate **21** using rhodium(II) trifluoroacetate [$Rh_2(tfa)_4$] is **22**; however, **23** is the predominant cycloadduct formed under $Rh_2(OAc)_4$ or rhodium(II) caprolactamate [$Rh_2(cap)_4$] catalysis.[36,54] A competing side-reaction is C=C insertion to give cyclopropane **24**. In a synthesis of platensimycin, the regioselectivity displayed by a substrate closely related structurally to **21** is reversed by the temporary introduction of a terminal halogen substituent on the tethered alkene dipolarophile (see Scheme 9 in "Applications to Synthesis" section).[55]

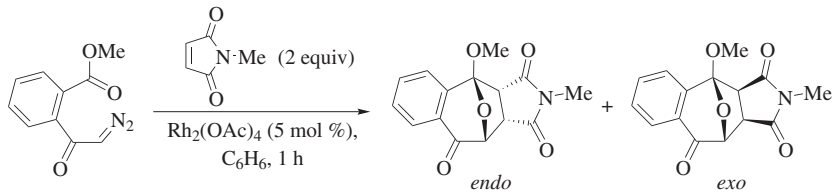


(Eq. 4)

Catalyst	**22–24** Yield (%)	**22/23/24**
$Rh_2(OAc)_4$	94	11:50:39
$Rh_2(cap)_4$	96	13:54:33
$Rh_2(pfb)_4$	87	38:14:48
$Rh_2(tfa)_4$	93	37:13:50

Stereoselectivity

Only one ylide geometry is possible in the simple achiral cyclic five- to seven-membered-ring carbonyl ylide intermediates **11** (Scheme 3). With symmetrical alkynes such as DMAD, this ylide geometry leads to a single cycloadduct **12** ($R^2 = R^3$). A single cycloadduct **12** ($R^2 \neq R^3$) or **13** ($R^2 \neq R^3$) is also observed with unsymmetrical alkyne and cyano dipolarophiles if the cycloaddition is completely regioselective. For alkene dipolarophiles presenting homotopic faces, such as *N*-phenylmaleimide, two diastereoisomers can arise, for example **14** and **15** ($R^2 = R^3$). The *exo*-product typically refers to the structure wherein the substituent on the original dipolarophile is *cis* to the ether bridge in the cycloadduct. With a 2-benzopyrylium-4-olate, the preference for *exo*- or *endo*-stereoselectivity can be controlled by the choice of catalyst used to decompose the diazocarbonyl precursor and/or the presence of a Lewis acid catalyst, typically a rare-earth metal triflate (Eq. 5).[56]

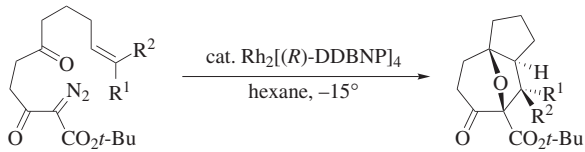


Conditions	*endo* + *exo* Yield (%)	*endo*/*exo*
reflux	70	11:89
$Yb(OTf)_3$ (5 mol%), rt	89	90:10

(Eq. 5)

The stereochemical outcomes with individual alkene geometrical isomers as dipolarophiles support a pericyclic pathway for the [3 + 2] cycloaddition. In the intramolecular examples in Eq. 6[57] (see Charts at the beginning of the Tabular Survey for full structures of the catalysts), due to geometric constraints, the alkene dipolarophiles tethered at the carbonyl group forming the ylide react completely regioselectively and exclusively in an *exo* fashion, in the sense that the tether ends up *cis* to the ether bridge. Stereospecificity in the cycloaddition then leads

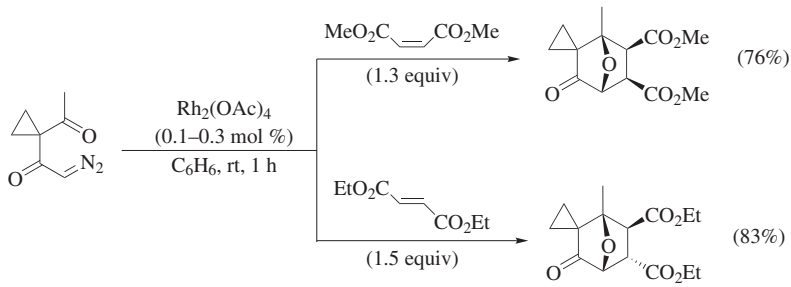
to a *trans* methyl group in the cycloadduct arising from the (*E*)-alkene, and to a *cis* methyl group in the cycloadduct arising from the (*Z*)-alkene. These examples also illustrate the maximum number of stereocenters (4) obtainable in an intramolecular carbonyl ylide cycloaddition from an achiral substrate.



R^1	R^2	Yield (%)	er
Me	H	53	90.0:10.0
H	Me	49	91.5:8.5

(Eq. 6)

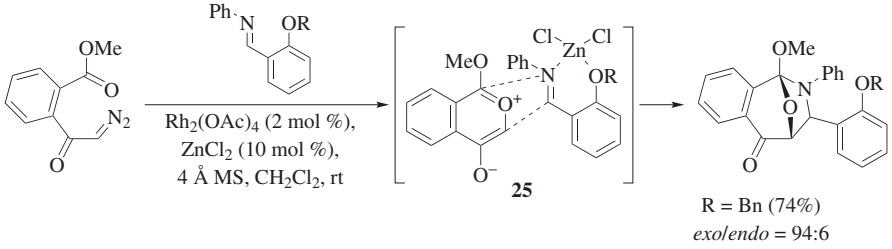
Intermolecular (Eq. 7)[58] cycloadditions also demonstrate concertedness.[58,59] The examples in Eq. 7 further illustrate the typically very high or complete *exo*-selectivity with maleate esters.[58] The orientation observed with the fumarate dipolarophile likely arises from minimization of non-bonded interactions between the ester and cyclopropane in the transition state.



(Eq. 7)

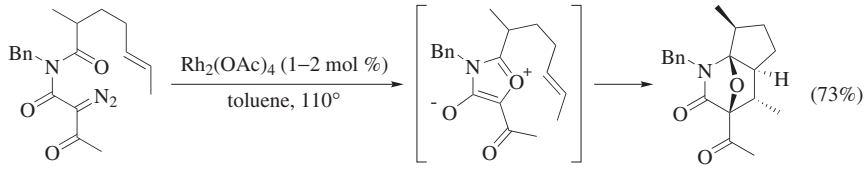
Although most, if not all, carbonyl ylide cycloadditions may well be concerted, non-concerted reaction pathways cannot be ruled out for more polarized dipolarophiles such as simple aldehydes, ketones, and imines under certain conditions. For concerted reactions, the extent of σ-bond formation at each terminus of the ylide with the dipolarophile in the transition state may vary considerably depending on the partners involved and the experimental conditions.[50] For example, computational studies for the cycloaddition of a 2-benzopyrylium-4-olate with an imine in the presence of $ZnCl_2$ catalyst indicate the formation of a weak complex between the ylide and the $ZnCl_2$-associated imine, followed by cycloaddition through an asynchronous process (Eq. 8).[44] The bond lengths in the transition structure **25** (R = Me) are 2.1 Å for the developing carbon–carbon bond and 3.2 Å for the carbon–nitrogen bond. In contrast, reaction in the absence of the Lewis acid catalyst, which does not generate a cycloadduct from the imine

in practice, proceeds by synchronous bond formation, with lengths of the developing bonds both at 2.4 Å.



(Eq. 8)

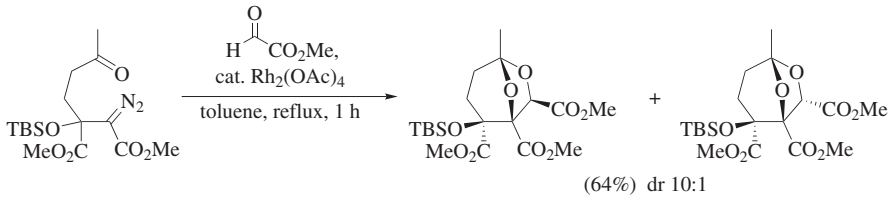
A pre-existing stereocenter in an ylide precursor causes the faces of the intermediate carbonyl ylide to be diastereotopic. The predominant sense and level of diastereoselectivity observed depends heavily on the substitution pattern of the substrate. As noted for Eq. 4 in the "Regioselectivity" section, geometric constraints dictate that tethering of a dipolarophile at a position within a cyclic ylide leads to intramolecular cycloaddition on the side where the tether is attached.[54,55,60–69] Intramolecular cycloadditions wherein the dipolarophile is tethered at the carbonyl group forming the ylide often occur with high diastereoselectivity where a stereocenter (or stereocenters), in the tether determines the preference for which face of the ylide reacts. Selectivity is seen when the stereocenter is present in a 3-,[68,70–76] 4-,[76–80] or 5-atom[81,82] -tether. For the isomünchnone cycloaddition in Eq. 9, minimization of steric interactions between the methyl group at the stereocenter and the benzyl group on nitrogen is a likely origin of the diastereoselectivity.[72]



(Eq. 9)

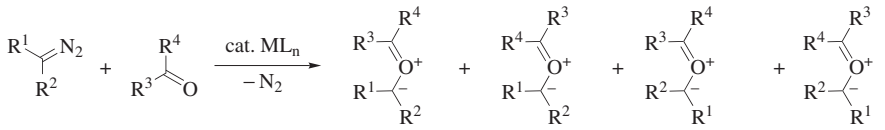
With simple achiral cyclic carbonyl ylides undergoing cycloaddition with achiral unsymmetrical dipolarophiles, such as monosubstituted alkenes ($R^3 = H$) or aldehydes, up to 4 diastereoisomers (**14**–**17**) may be generated (Scheme 3). If a carbonyl ylide intermediate and/or dipolarophile are chiral, then diastereofacial selectivity becomes important. An example that illustrates these aspects is the intermolecular cycloaddition of a keto diester with methyl glyoxylate (Eq. 10), for which two of eight possible cycloadducts are isolated.[83,84] With such an electron-deficient dipolarophile, the cycloaddition is likely to be type I ($LUMO_{dipolarophile}$-controlled), and such a highly polarized dipolarophile leads to

the high regioselectivity observed. The presence of the tetrasubstituted stereocenter in the carbonyl ylide is the likely origin of the predominant *exo*-orientation in the cycloaddition, as a keto group at that position leads to *endo*-selectivity.[85] Finally, diastereofacial selectivity likely originates from the dipolarophile preferentially approaching the ylide on the side opposite to the sterically demanding silyloxy substituent.

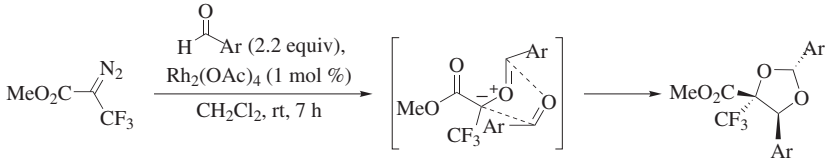


(Eq. 10)

For acyclic ylide generation, up to four geometrically distinct planar carbonyl ylide intermediates are possible if the diazo- and carbonyl-containing precursors are not symmetrically substituted (Scheme 5).[86] However, a judicious choice of substrates and/or reaction conditions can lead to the formation of mainly one cycloadduct, likely arising from a single carbonyl ylide isomer (Eqs. 11[87] and 12[88]). In Eq. 11, the cycloadduct is derived from the sickle-shaped (with respect to ester and aryl groups) carbonyl ylide shown. This ylide, with the ester carbonyl in an s-*cis* rather than an s-*trans* conformation, is computationally determined to be the most stable of the possible carbonyl ylides.[87] The aldehyde dipolarophile, shown as approaching above the ylide in Eq. 11, orients its aryl group toward the ester and away from the trifluoromethyl group.

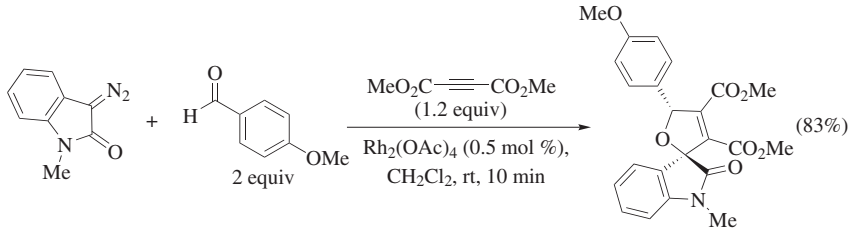


Scheme 5



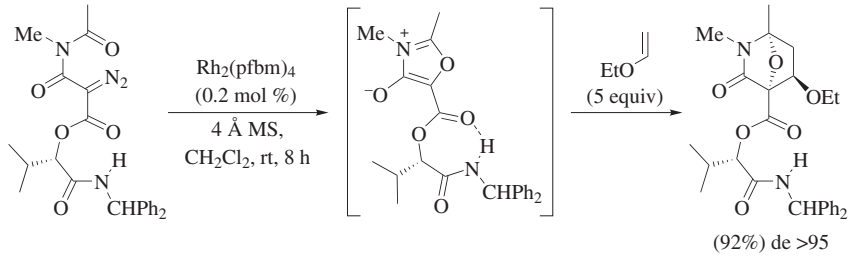
Ar	Yield (%)
4-ClC_6H_4	82
4-FC_6H_4	89
4-$MeOC_6H_4$	95

(Eq. 11)



(Eq. 12)

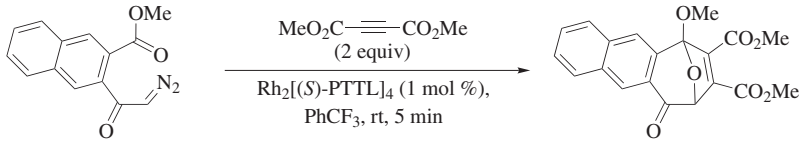
Asymmetric Cycloadditions. Diastereofacial selectivity in carbonyl ylide cycloadditions has been achieved using chiral-auxiliary-bearing ylides in the case of diazoimide-derived isomünchnones,[89–92] or chiral non-racemic dipolarophiles such as vinyl sulfoxides.[93] In the isomünchnone cycloaddition shown in Eq. 13, the valine-derived chiral auxiliary is located at an ester at the diazo carbon, and is readily removed after cycloaddition by reaction of a primary amine at the ester group.[91] The auxiliary induces high diastereofacial selectivity in the cycloaddition, and the complete regioselectively and *endo*-selectivity with a vinyl ether as dipolarophile is also seen with analogous achiral ester-substituted diazoimides.[94] Considerably reduced diastereofacial selectivities occur with structurally related chiral auxiliaries where the amide N–H is absent. Together with computational studies, these observations suggest that a hydrogen bond is important for effective asymmetric induction.[91]



(Eq. 13)

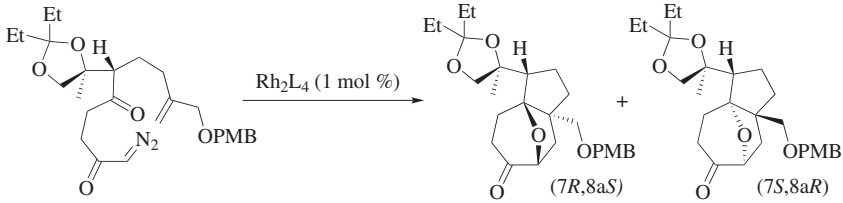
Enantioselective cycloadditions of carbonyl ylides derived from diazo compounds have been achieved by two conceptually different approaches. In the first approach, a chiral, non-racemic catalyst decomposes the diazo substrate to form the ylide, and then likely remains associated with the ylide to bias facial selectivity in the ensuing cycloaddition.[36] In specific cases, high levels of asymmetric induction are achieved for both intra- and intermolecular cycloadditions of non-aromatic cyclic carbonyl ylides and intermolecular cycloadditions of oxidopyryliums (Eqs. 6 and 14).[48,57,95–99] However, the origins of asymmetric induction in this approach are not currently understood, but rather arise from a complex blend of electronic and steric effects from the dipole and dipolarophile,

together with the specific catalyst and solvent.



(Eq. 14)

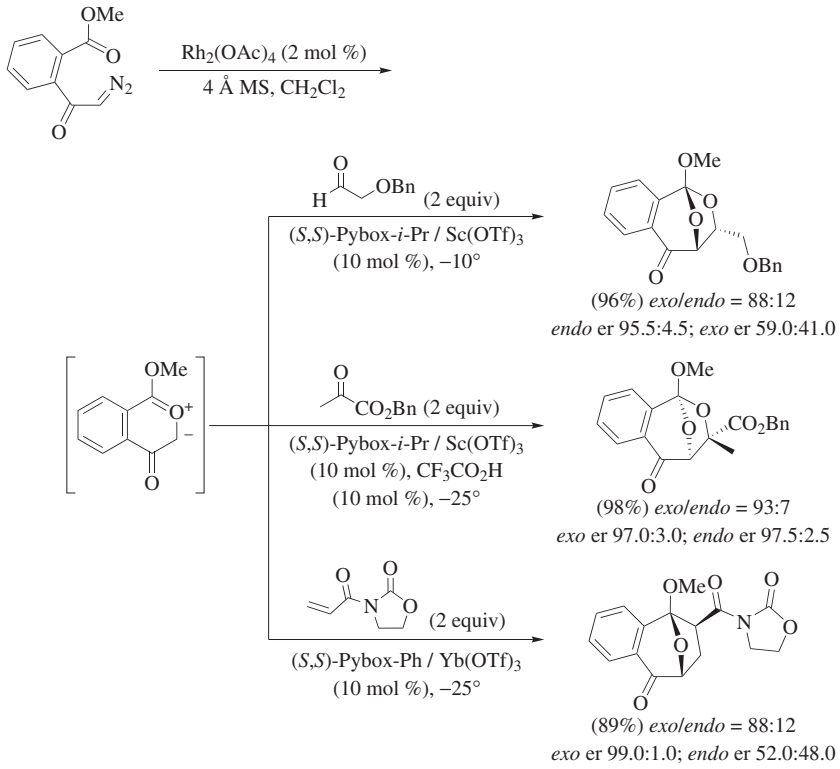
Chiral catalysts can override a substrate bias when dealing with a single enantiomer of a substrate[70] (Eq. 15).[74,76] Under achiral catalysis with $Rh_2(OAc)_4$, the diastereoselectivity originates from minimizing interactions between the dioxolane and PMB ether groups.



Rh_2L_4	Solvent	Temp (°)	Yield (%)	(7*R*,8a*S*)/(7*S*,8a*R*)
$Rh_2(OAc)_4$	CH_2Cl_2	0	61	1:3
Rh_2[(*S*)-DOSP]$_4$	CH_2Cl_2	0	60	1:4
Rh_2[(*S*)-BPTV]$_4$	CH_2Cl_2	0	59	1:1.4
Rh_2[(*S*)-BPTV]$_4$	$PhCF_3$	0	54	1.1:1
Rh_2[(*S*)-BPTV]$_4$	$PhCF_3$	–40	82	1.6:1

(Eq. 15)

In the second approach to enantioselective cycloadditions of carbonyl ylides, an achiral catalyst is used to decompose the diazo substrate and enantioselectivity arises from the presence of a chiral, non-racemic Lewis acid catalyst, typically derived from a lanthanide triflate and a 2,6-bis(oxazolinyl)pyridine (Pybox) ligand. Good enantioselectivities are observed with 2-benzopyrylium-4-olates and dipolarophiles capable of bidentate coordination to the Lewis acid, such as α-aryloxy aldehydes, pyruvates, and 3-(2-alkenoyl)-2-oxazolidinones (Scheme 6).[100–102] In these cases, asymmetric induction likely arises from coordination of the Lewis acid with the dipolarophile, thus lowering the LUMO of the dipolarophile.[44] Intriguingly, good levels of asymmetric induction can also be observed when using enol ethers as dipolarophiles, together with 2-benzopyrylium-4-olates or non-aromatic carbonyl ylides, and pybox europium(III) triflate or nickel(II) binaphthyldiimine as Lewis acid catalysts. These cycloadditions have been computationally determined to be $LUMO_{dipole}$–$HOMO_{dipolarophile}$ controlled, which implies that coordination of the chiral Lewis acid to the dipole is involved in the enantiodifferentiating process.[103,104]

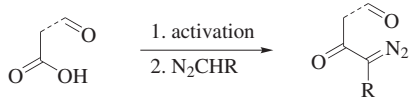


Scheme 6

SCOPE AND LIMITATIONS

Structural Scope at the Diazo Group

The diazo functionality is normally flanked by at least one carbonyl group to stabilize the cycloaddition substrate and enhance the electrophilicity of the intermediate metallocarbene. With just one carbonyl group flanking the diazo group, the other substituent (R in **26**, Eq. 16) is often nothing more than H. Such substrates are typically accessed using the reaction of diazomethane with acid chloride or mixed anhydride precursors, or via deformylative diazo transfer (see "Availability of α-Diazocarbonyl Substrates" section). The flanking carbonyl group is commonly, but not always (Eq. 10), destined to reside endocyclic if the reaction proceeds through a cyclic carbonyl ylide (Eqs. 3–5, 7, 8, 14, 15).

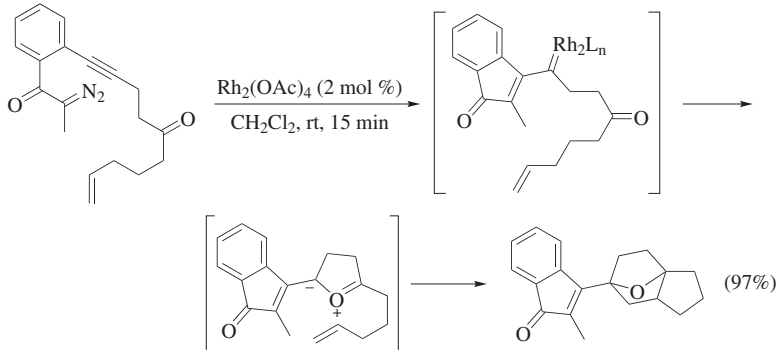


26 (Eq. 16)

Less commonly, alkyl groups are present on the diazo carbon (**26**, R = alkyl), but their preparation can require higher diazoalkanes, which are both more

difficult to access and less stable than diazomethane. Nevertheless, the resulting substrates undergo cycloaddition via ylide formation in preference to adjacent C–H insertion.[105,106] Doubly stabilized α,α′-dicarbonyl diazo substrates are also quite common (Eqs. 2, 6, and 9) and the additional stability can provide greater scope in assembling the starting material (see "Availability of α-Diazocarbonyl Substrates" section).

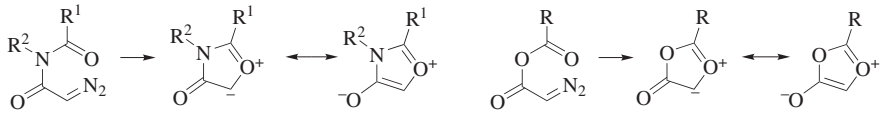
One interesting variant to generate the metallocarbene precursor involves a diazo substrate from which the first-formed metallocarbene initially interacts with an alkyne to form a vinyl metallocarbene prior to ylide generation (Eq. 17).[107,108]



(Eq. 17)

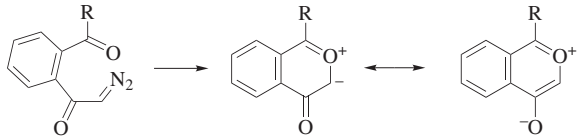
Scope of the Carbonyl Group Forming the Ylide

With regard to the carbonyl partner forming the ylide, the scope is quite wide. In the intramolecular variant, the carbonyl can be an aldehyde, ketone (most common), ester, amide, or imide. However, for reasons currently not understood, some esters do not participate, especially when the target ylide is non-aromatic.[109] For both the intra- and intermolecular cycloadditions using cyclic carbonyl ylides, similar factors will clearly determine the breadth and limitations in the ylide-forming step. The five- to seven-membered-ring ylides have been generated in situ.[110,111] However, as expected, the efficiency generally diminishes with the larger rings.[112,113,113a] In the "Tabular Survey", reactions that proceed by the carbonyl group initially cyclizing to generate an aromatic ylide intermediate are listed in separate sub-sections from otherwise related cycloadditions involving non-aromatic carbonyl ylides. Cyclization of imides or anhydrides can give five-membered-ring aromatic mesoionic ylide intermediates: isomünchnones and 1,3-dioxoliums (Scheme 7), respectively, with the former being considerably more common.



Scheme 7

Six-membered-ring ylides can also possess aromaticity. By far the most common of such intermediates in cycloadditions are the benzo-fused (oxido)pyryliums (Scheme 8), although examples of fused isoxazoles are also known.[114]



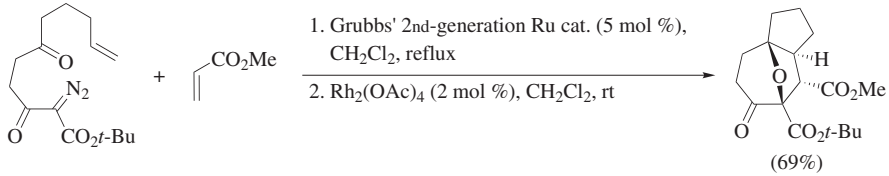
oxidopyrylium ylide

Scheme 8

Intermolecular ylide-forming processes are currently known for aldehydes, ketones, and imides. Unless the carbonyl-containing substrate forming the ylide is also intended to function as the dipolarophile, care needs to be taken to avoid the putative intermediate metallocarbene reacting directly with the dipolarophile, rather than via the desired ylide.

Scope of the Dipolarophile

For the intramolecular cycloaddition, the dipolarophile can be an unactivated C=C π-bond, such as a tethered simple alkene (Eqs. 4, 6, 9, 15, 17),[54,58,60,64,69,70,72,75,76,95,108,115–123] allene,[124] alkyne (Eq. 1),[57,114,125–130] aryl-substituted alkene,[121,122] or alkenyl halide.[55] The dipolarophile C=C π-bond can also be activated, such as in an α,β-unsaturated ester (Eq. 18),[119,121,122,127] α,β-unsaturated aldehyde,[121,122] or an alkenyl sulfonic ester,[68] or be part of an aromatic heterocycle, such as a furan,[131–134] thiophene,[131,134,135] or indole.[61,118,133,136–142] A ketone also functions as a dipolarophile in the intramolecular process.[54] A significant issue for intramolecular cycloadditions is construction of the multifunctionalized substrate. Alkene cross-metathesis using unsaturated diazocarbonyl substrates with α,β-unsaturated carbonyl compounds or styrenes is a useful way to create diversity in the tethered dipolarophile (Eq. 18).[121,122] The cross-metathesis and cycloaddition chemistry can be carried out as a one-flask operation by adding the rhodium catalyst to facilitate carbonyl ylide formation after the cross-metathesis is completed.

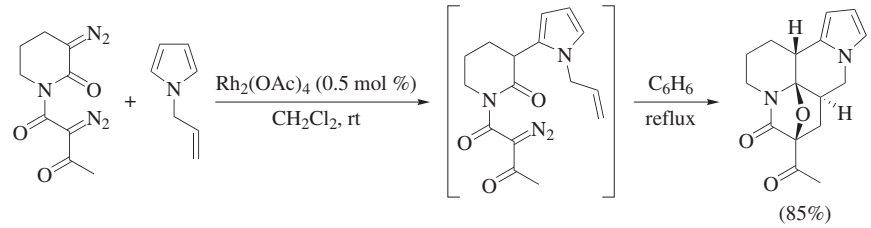


(69%)

(Eq. 18)

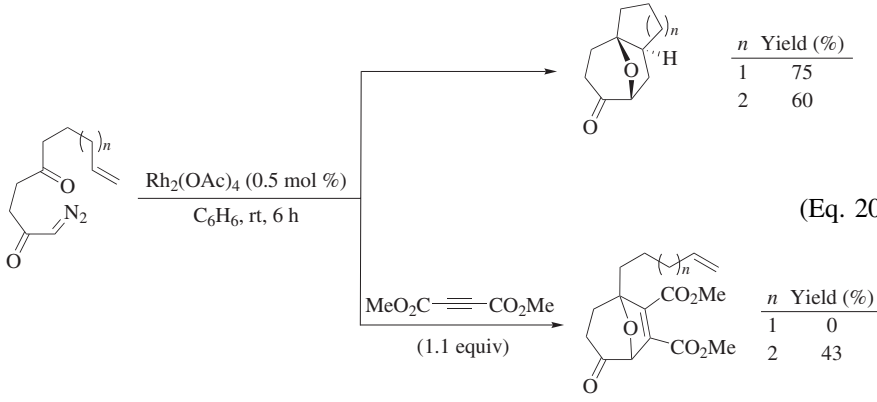
Starting from a bis-diazoimide, a $Rh_2(OAc)_4$-catalyzed one-flask intermolecular formal C–H insertion on *N*-allylpyrrole followed by tandem intramolecular carbonyl ylide formation and cycloaddition involving the remaining diazo group

has been achieved (Eq. 19).[143] This reaction is an interesting example of a powerful strategy for intramolecular cycloadditions in which the catalyst is involved in both substrate assembly and cycloaddition.



(Eq. 19)

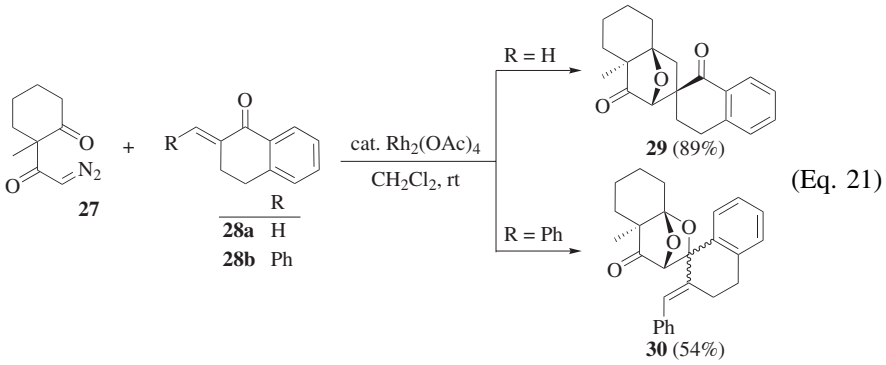
The tether between the ylide and the dipolarophile must allow satisfactory or suitable alignment for successful cycloaddition. A two-atom tether does not support intramolecular cycloaddition, whereas a three-atom tether leading to five-membered ring formation is normally best.[42,95] Six-membered ring formation from a four-atom tether occurs in satisfactory yield,[57,126] and seven-membered ring formation is known[81,82] but rare (cf. Scheme 13). An example of the slower rate of cycloaddition involving a four-carbon tether compared with that involving a three-carbon tether is found with unsaturated 1-diazo-2,5-diketones (Eq. 20).[43] Both substrates undergo tandem carbonyl ylide formation–intramolecular cycloaddition to give cycloadducts. However, in the presence of DMAD only the ylide derived from the four-carbon-tethered substrate is intercepted in an intermolecular cycloaddition, outcompeting the intramolecular process.



(Eq. 20)

For intermolecular cycloadditions, the dipolarophile scope is rather wide; simple alkenes are the only π-containing systems known to fail.[95,104] The following are all viable dipolarophiles that participate in cycloaddition at a carbon–carbon double bond: cycloalkenes such as cyclopentene with a strained ylide,[58] [60]fullerene,[144–146] strained alkenes such as norbornenes,[58,96]

methylenecyclopropanes,[147] and cyclopropenes,[148] allenes,[105,149] conjugated dienes,[150] styrenes,[45,48,96] stilbenes,[59] heteroatom-substituted electron-rich and -poor alkenes[45] such as allyl alcohol,[104] enol ethers (Eq. 13),[45,94,103,104,151–154] ketene acetals,[58,104,155–157] alkenyl sulfones,[154,156–159] sulfoxides,[93] indoles,[160,161] α,β-unsaturated esters (Eq. 7),[58,140,162–164] α,β-unsaturated lactones,[75] α,β-unsaturated amides, α,β-unsaturated imides (Eq. 5,[56] Scheme 6), and acrylonitrile.[47,58,75,106,156,165] α,β-Unsaturated ketones may undergo cycloaddition at either the C=C or C=O π-bond, or reaction may be competitive at both positions, as seen with some quinones,[166] resulting in mixtures. Reaction mainly or exclusively at the C=C π-bond is found with simple β-unsubstituted α,β-unsaturated ketones, such as methyl vinyl ketone,[108,154,167,168] α-methylene indanone, and tetralone,[169–171] as well as with cyclopentenones,[58,156,172–176] and cyclohexenones.[58,156,170,177] If the α,β-unsaturated ketone bears a further conjugating substitutent, such as an aryl ring, at the β-position then cycloaddition occurs at the C=O π-bond.[178–180] For example, reaction of the five-membered-ring ylide derived from diazo dione **27** with α,β-unsaturated ketone **28a** (R = H) affords spiro adduct **29**, with cycloaddition having occurred regioselectively at the C=C bond (Eq. 21).[169] However, chemoselectivity toward C=O cycloaddition can also be achieved with arylidenetetralone **28b** possessing a phenyl substituent on the C=C bond. The latter leads to the spirodioxolane **30** with high chemo- and regioselectivity,[181] albeit poor diastereoselectivity (2:3).



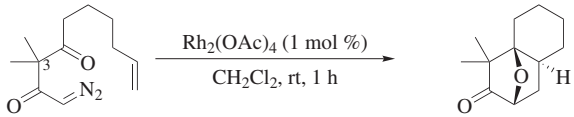
(Eq. 21)

Similarly wide scope is seen with alkynes as dipolarophiles. Cycloaddition has been observed with simple alkynes such as propyne,[105] aryl acetylenes,[46,48,182] alkoxy-[48,151] and sulfone-[183] substituted alkynes, as well as conjugated acetylenic esters (Eqs. 3, 12,[88] 14 and 20[43]),[112,113,164,184–186] and ketones.[47,106,165] Aside from dipolarophile reactivity at the C=O bond of certain α,β-unsaturated ketones mentioned above, simple ketones,[179,187,188] including α-keto esters (Scheme 6),[100,101] are also viable substrates. Cycloaddition with a C=O bond is seen for many simple aldehydes (Eq. 11[87] and Scheme 6),[45,86,99,101,112,176,189–193] including formaldehyde (see Scheme 18 in "Applications to Synthesis" section),[105] pivalaldehyde,[194] and glyoxylates (Eq. 10).[83–85] Chemoselective cycloaddition at the aldehyde group is seen for aldehydes conjugated with

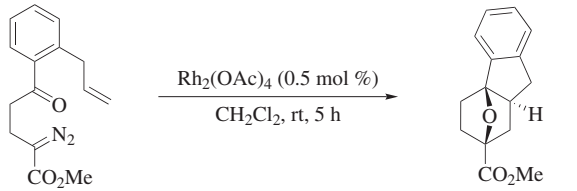
alkenyl-[42,176] or alkynyl[106]-functionality. Cycloadditions occur with imines (Eq. 8),[44,92,119,195–197] and with the C=N functionality in isocyanates[198] and thioisocyanates.[199] The cyano functional group, when attached directly to an ester group, participates in dipolar cycloadditions with carbonyl ylides,[45,112,113,119,183] as do phosphaalkynes (Eq. 42),[200] CS_2,[201] azodicarboxylates (Eq. 35),[106,202,203] and singlet oxygen.[203]

Intramolecular Cycloadditions of Cyclic Carbonyl Ylides

Intramolecular Cycloadditions of Cyclic Carbonyl Ylides from Ketones. Viable cycloadditions of five-membered-ring ylides derived from 1-diazo-2,4-dicarbonyl substrates require tetrasubstitution at the 3-position (Eq. 22),[58] so as to avoid collapse of the ylide by proton transfer (see Eq. 52 in "Limitations and Side-Reactions"). Such substitution is not required if the carbonyl group flanking the diazo substituent will be exocyclic following cycloaddition (Eqs.17 and 23).[120]

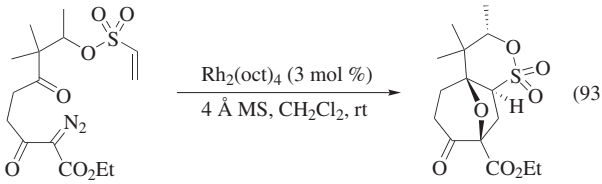


(Eq. 22)



(Eq. 23)

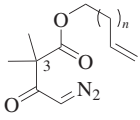
Intramolecular cycloadditions of six-membered-ring ylides derived from ketones are more common (Eqs. 4, 6, 10, 15, 18, and 20), and constitute the key-step in several natural product syntheses (see Schemes 9–13 in "Applications to Synthesis" section). Eq. 24 illustrates the use of a tethered alkenyl sulfonate as the dipolarophile, with a stereocenter in the tether inducing high diastereofacial selectivity in the cycloaddition.[68] Intramolecular cycloadditions of ketone-derived cyclic ylides that contain more than six atoms in the tether have not been reported.



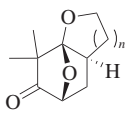
(Eq. 24)

Intramolecular Cycloadditions of Cyclic Carbonyl Ylides (Pyryliums) from Esters. Only a few examples have been reported for intramolecular cycloadditions of five-membered-ring carbonyl ylides wherein ester groups serve as the source of the ylide oxygen.[60,155,157] Eq. 25[204] illustrates

substrates with tetrasubstitution at the 3-position, in this case *gem*-dimethyl, which is typically needed for successful five-membered-ring carbonyl ylide generation–cycloaddition. High *exo* selectivity is evident as the ester-linked tethers end up *cis* to the ether bridges in the cycloadducts.



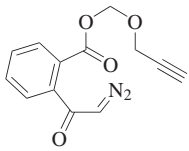
$Rh_2(OAc)_4$ (0.6 mol %)
C_6H_6, 80°, 3 h



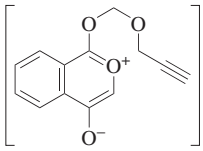
n	Yield (%)
1	56
2	62

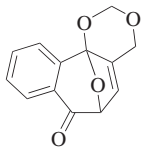
(Eq. 25)

There are more examples of intramolecular cycloadditions of six-membered-ring ester-derived carbonyl ylides[114,119,122,125,130,205–209] compared with the corresponding five-membered-ring systems, although the former have been reported only wherein the ylide is aromatic (a pyrylium, Scheme 8 and Eq. 26[125]). The reaction in Eq. 27 illustrates a less common arrangement for intramolecular cycloaddition, wherein the dipolarophile is tethered at the diazo group.[119]



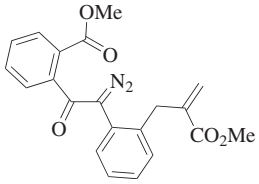
$Rh_2(OAc)_4$ (3 mol %)
CH_2Cl_2, rt, 5 h



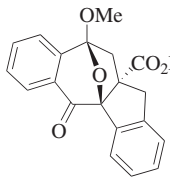


(74%)

(Eq. 26)

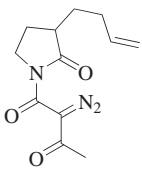


cat. $Rh_2(OAc)_4$
hexane, 80°

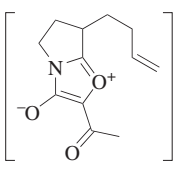


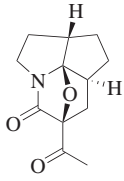
(68%) (Eq. 27)

Intramolecular Cycloadditions of Cyclic Carbonyl Ylides (Isomünchnones) from Imides. Reaction of suitably assembled unsaturated diazoimides in the presence of a transition-metal catalyst leads to tandem ylide formation–intramolecular cycloaddition. Most commonly, the imidic nitrogen becomes part of a five-membered-ring ylide intermediate, an aromatic isomünchnone species (Scheme 7).[61–63,66,72,73,75,77,79,128,129,132,133,136,143,164,210–212] Eqs. 28 and 29 illustrate intramolecular cycloadditions proceeding through isomünchnone intermediates in the stereocontrolled generation of polycyclic systems, which arise from a butenyl-substituted pyrrolidinone, and from an imidic *N*-linked dipolarophile, respectively.[66,211]



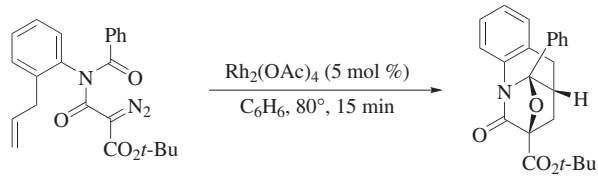
$Rh_2(OAc)_4$ (1 mol %)
C_6H_6, 80°, 3 h





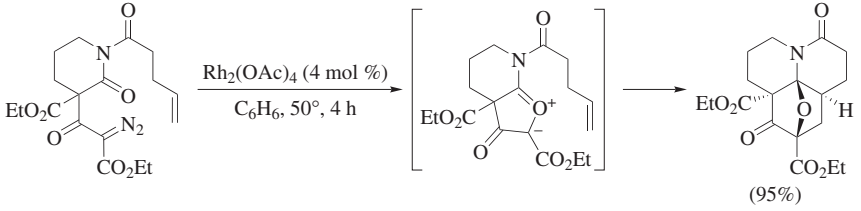
(88%)

(Eq. 28)

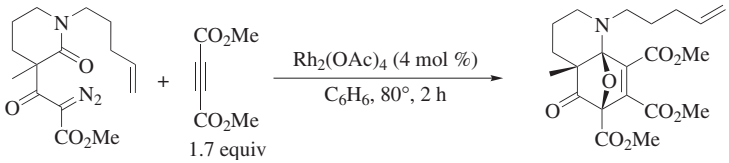


(95%) (Eq. 29)

Only a few substrates are constructed so as to proceed by way of the imidic nitrogen becoming exocyclic in the cyclic ylide intermediate.[118,131,134,135,137–139,141,142,213–215] In these cases, the dipolarophile is attatched by *N*-acylation of an α,α-disubstituted piperidinone. Eq. 30 provides an example wherein formation of the tetracyclic adduct is formed with complete diastereocontrol.[214] Interestingly, although a few unsaturated amides and lactams are known to undergo the cycloaddition process,[118] a substrate similar to that shown in Eq. 30, but having no carbonyl substituent present in the tether, fails to undergo intramolecular cycloaddition. Intermolecular cycloaddition with DMAD shows that the dipole forms (Eq. 31), but in the absence of an external dipolarophile only substrate decomposition and unspecified side-reactions are observed. Computational analysis leads to the conclusion that the presence of the carbonyl group in the dipolarophile tether helps to relieve steric congestion in the transition state.[214]



(Eq. 30)



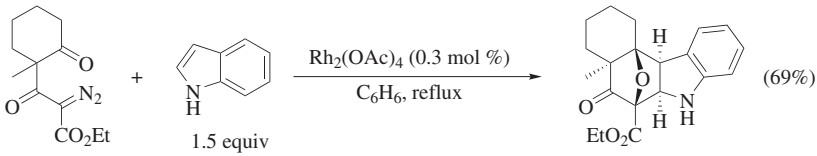
(Eq. 31)

Intermolecular Cycloadditions of Cyclic Carbonyl Ylides

Because the synthetic limitations in assembling substrates for intramolecular cycloadditions are often not a problem for conducting intermolecular cycloadditions, significantly greater diversity is found in the range of dipolarophiles available for the latter process. These dipolarophiles include alkenes, allenes, alkynes, ketones, aldehydes, imines, and nitriles.

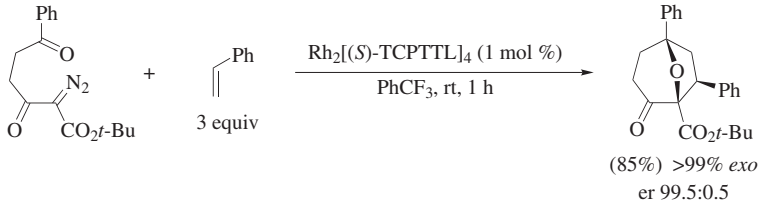
Intermolecular Cycloadditions of Cyclic Carbonyl Ylides from Ketones. Many examples have been reported of ketone-derived five-, six-, and occasionally seven-membered-ring carbonyl ylide formation followed by [3 + 2] cycloaddition

(Tables 9–11, Eqs. 2, 3, 7, 10, 20, and 21). However, intermolecular cycloadditions of a ketone- or aldehyde-[119] derived pyrylium are rare (Table 10B).[216] Similar to the intramolecular process, intermolecular cycloadditions of five-membered-ring ylides derived from 1-diazo-2,4-dicarbonyl substrates require tetrasubstitution at the 3-position to avoid collapse of the ylide by proton transfer (see also Eq. 52). Eq. 32 illustrates a regioselective cycloaddition with indole as the dipolarophile, and which occurs on the less-hindered face of the ylide with *exo*-stereoselectivity.[161]



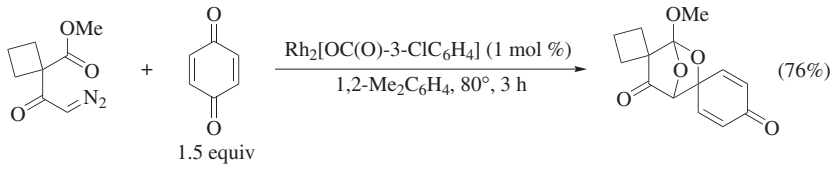
(Eq. 32)

Highly enantioselective intermolecular cycloadditions of ketone-derived cyclic carbonyl ylides have been achieved with a variety of styrenes, alkynes, and aromatic aldehydes, typically using chiral α-amino-acid-derived tetracarboxylate dirhodium catalysts (Eq. 33).[48,96,97,99] The presence of a sterically demanding ester group at the diazo carbon is important for high asymmetric induction with a range of dipolarophiles.



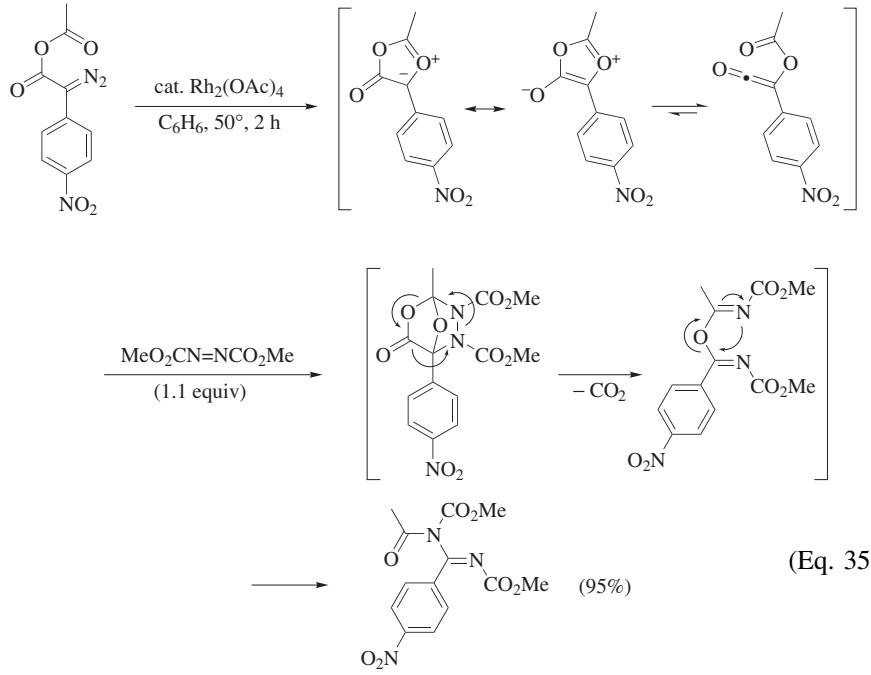
(Eq. 33)

Intermolecular Cycloadditions of Cyclic Carbonyl Ylides from Esters or Anhydrides. Only a few examples have been reported for the formation of five-membered-ring carbonyl ylides using ester carbonyl groups followed by intermolecular cycloaddition (see Scheme 19 in "Applications to Synthesis" section).[112,155,157,166,186] The reaction in Eq. 34 illustrates chemoselectivity for the C=O π-system in the quinone dipolarophile, which also undergoes regioselective cycloaddition.[166]



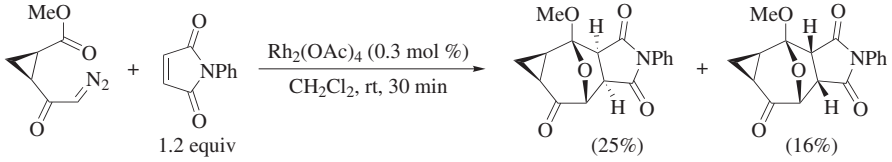
(Eq. 34)

Aryldiazoacetic anhydrides undergo $Rh_2(OAc)_4$ or π-allylpalladium-complex-catalyzed generation of five-membered-ring mesoionic 1,3-dioxolium-4-olates (Scheme 7, Eq. 35). Despite being in equilibrium with the more stable acyloxyketenes, the 1,3-dioxolium-4-olates undergo [3 + 2] cycloaddition with a range of dipolarophiles.[202,203,217–219] Under the reaction conditions, loss of CO_2 from the cycloadducts is common. With azodicarboxylate dipolarophiles, N–N cleavage also occurs followed by Mumm rearrangement of the resulting imidoyl imidates to give triacylbenzamidine derivatives as the final products (Eq. 35).[203,217]

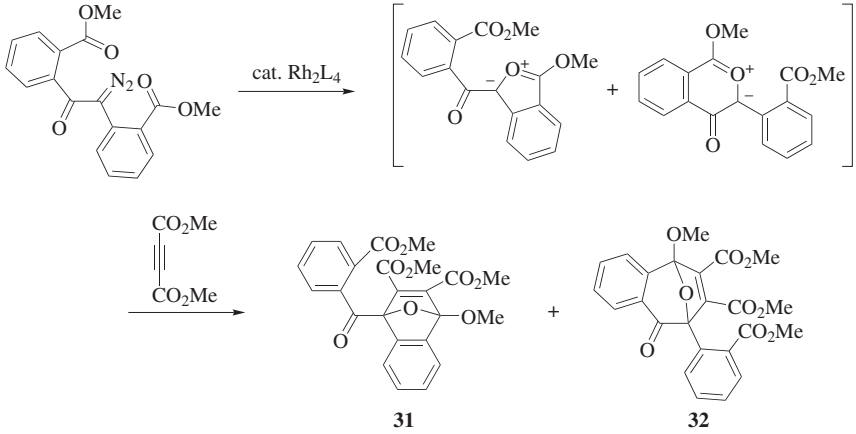


(Eq. 35)

Only a few intermolecular cycloadditions involving six-membered-ring non-aromatic carbonyl ylides that are formed using ester carbonyl groups have been reported (Eq. 36,[220] Scheme 20 in "Applications to Synthesis" section).[47,98,151,165,221] The majority of intermolecular cycloadditions involving six-membered-ring carbonyl ylides formed using ester carbonyl groups involve (benzo)pyrylium ylides [Scheme 8 (R = alkoxy), Eq. 8], with which a wide range of dipolarophiles have been used successfully. The influence of catalysts on the *exo*/*endo* stereoselectivity (Eq. 4) and enantioselectivity has been studied extensively (Eq. 15, Scheme 6). The ratio of cycloadducts arising from competitive generation of ester-derived five- (product **31**) and six- (product **32**) membered-ring carbonyl ylides depends on the catalyst used (Eq. 37),[119] the former ylide being equivalent to an isobenzofuran.[222]



(Eq. 36)

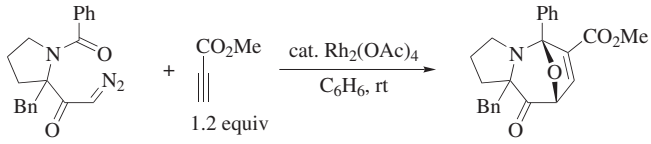


31 **32**

			Yield (%)		
Rh_2L_4	Solvent	Temp	**31**	**32**	**31/32**
$Rh_2(OAc)_4$	toluene	110°	68	17	4:1
$Rh_2(tfa)_4$	—	—	—	—	2:1
$Rh_2(cap)_4$	—	—	78	5	15.6:1

(Eq. 37)

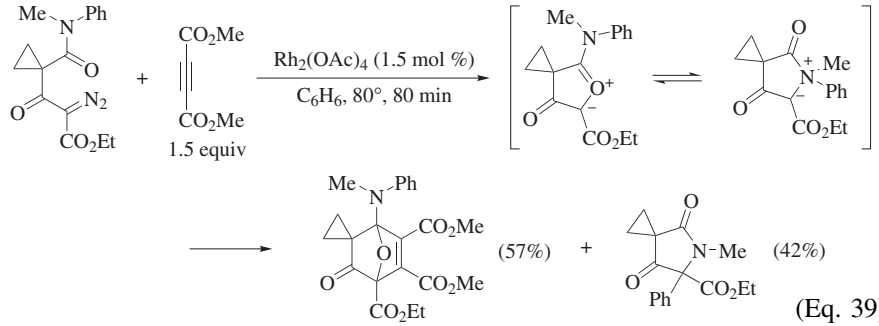
Intermolecular Cycloadditions of Cyclic Carbonyl Ylides from Amides. Only a few examples of the formation of cyclic carbonyl ylides using amide carbonyl groups and their subsequent cycloadditions have been reported.[34,107,108,111,155,208,209,214,223–228] Isolated carbamate and urea-type examples are also known.[223,229] Eq. 38 illustrates a regioselective cycloaddition using an amide carbonyl group to form the ylide with methyl propiolate as the dipolarophile. The reaction also occurs with diastereofacial selectivity on the carbonyl ylide intermediate to generate a single cycloadduct, for which the sense of diastereoselection is undetermined.[223]



(80%) (Eq. 38)

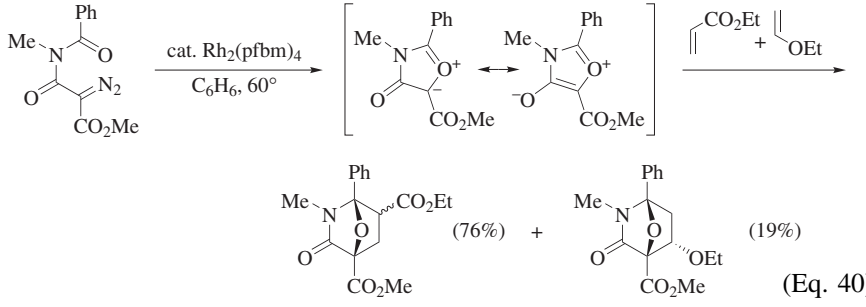
Other successful examples with amides include lactams wherein the diazo functionality is attached at the α-position, and for six- and seven-ring systems,

wherein the nitrogen becomes part of the cyclic ylide intermediate. However, for the latter, products derived from dipole interconversion to an azomethine ylide can occur for certain substrates (Eq. 51). Also, products derived from ammonium ylide formation can compete with those from carbonyl ylide generation in cases where the nitrogen atom is not part of a pre-existing ring and is destined to become exocyclic to the carbonyl ylide (Eq. 39).[37]

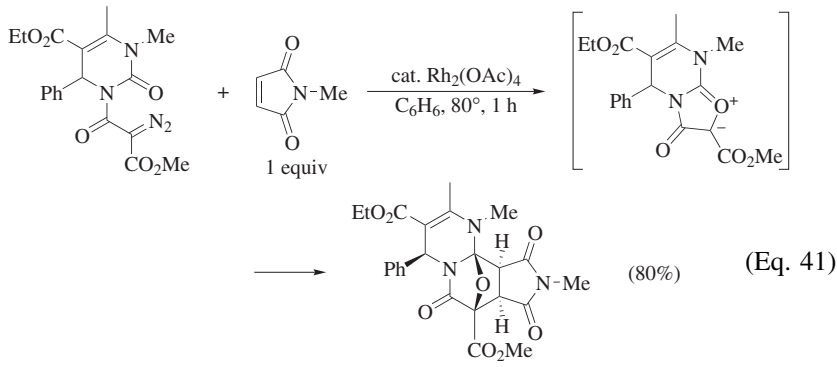


(Eq. 39)

Intermolecular Cycloadditions of Carbonyl Ylides (Isomünchnones) from Imides. Many intermolecular cycloaddition reactions of five-membered-ring carbonyl ylides (isomünchnones, Scheme 7, Eqs. 40 and 41) from imides have been reported, but only a few examples are known for the corresponding six-[164,223,230,231,231a,231b] and seven-membered-[111] ring ylides. A cycloaddition catalyzed by rhodium(II) perfluorobutyramidate [$Rh_2(pfbm)_4$] involving two competing dipolarophiles (Eq. 40) occurs regioselectively in both cases and *endo*-selectively for the enol ether.[94] The comparable reactivity indicates similar FMO energetics for both electron-rich and electron-deficient dipolarophiles in the isomünchnone cycloaddition. A phenyl substituent induces complete diastereofacial selectivity in the cycloadditions of a dihydropyrimidine-fused isomünchnone, which also occurs with complete *exo*-stereoselectivity with *N*-methylmaleimide as the dipolarophile (Eq. 41).[63] The intermediate isomünchnone precipitates in 88% yield when the same reaction is carried out in the absence of a dipolarophile, and the isolated isomünchnone also undergoes catalyst-free cycloaddition with *N*-methylmaleimide (CH_2Cl_2, rt, 20 minutes, 82%).

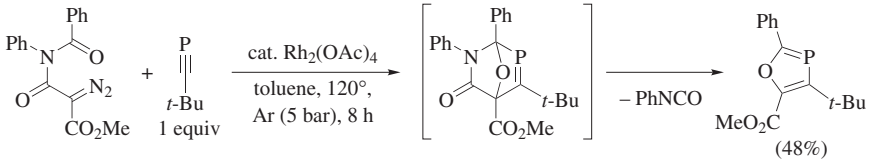


(Eq. 40)

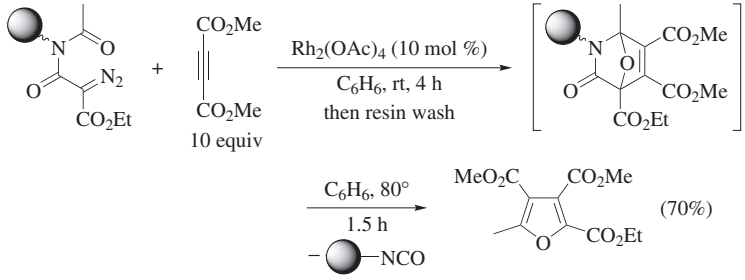


(Eq. 41)

The intermolecular 1,3-dipolar cycloaddition of isomünchnones with alkynes or phosphaalkynes[200] is typically followed by extrusion of an alkyl or aryl isocyanate to give substituted furans or 1,3-oxaphospholes, respectively (Eq. 42). For the synthesis of furan-based combinatorial libraries, "traceless" solid-phase versions of this process involve diazoimides assembled on TentaGel™ or Wang resin and linked through the imido nitrogen.[232–234] These diazoimides undergo Rh_2L_4-catalyzed isomünchnone formation and cycloaddition with alkyne dipolarophiles followed by thermally induced cycloreversion to release the furan, leaving behind the isocyanate-bound resin (Eq. 43).[232]



(Eq. 42)

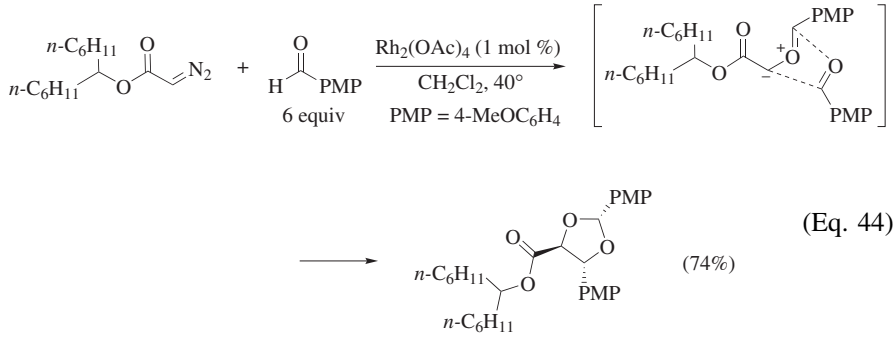


(Eq. 43)

Generation of Acyclic Carbonyl Ylides from Aldehydes, Ketones, or Imides and Their Cycloadditions

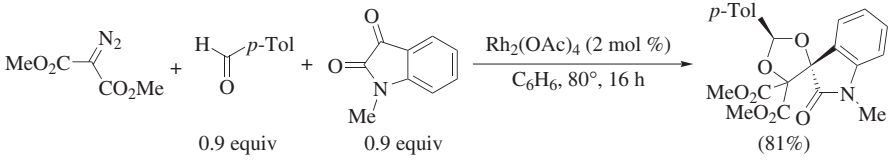
The majority of acyclic carbonyl ylide cycloadditions are intermolecular. Although some cycloadditions involving acyclic carbonyl ylides occur with high stereocontrol (Eqs. 11, 12, 44–47), acyclic ylides can potentially exist as and

react via several geometric isomers (Scheme 5),[86] which may contribute to poor diastereocontrol. Several examples of acyclic carbonyl ylide cycloadditions involve the dipole carbonyl source also functioning as the dipolarophile component to give 1,3-dioxolanes (Eqs. 11 and 44).[86,189,235] In Eq. 44,[86] the cycloadduct isolated as a single isomer derives from the sickle-shaped carbonyl ylide shown. This ylide is computationally determined to be the most stable of the four possible geometrically distinct planar carbonyl ylides, likely due to minimization of electronic repulsions. The diastereoselectivity in this cycloaddition probably arises from the aldehyde dipolarophile, shown as approaching above the ylide in Eq. 44, orienting its aryl group away from the sterically demanding (dicyclohexyl)methoxy group of the ester.



(Eq. 44)

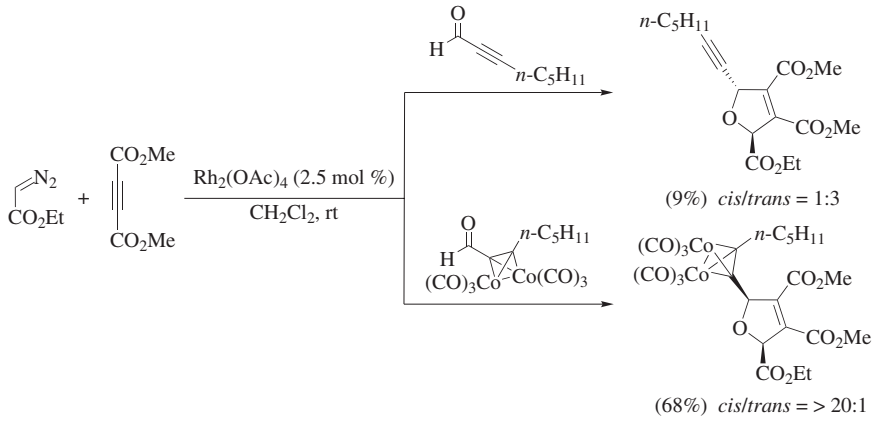
Perhaps surprisingly, given the potential for alternative reaction pathways, three component coupling has been successfully demonstrated in a number of cases. In the three-component process, dipolarophiles that have successfully been used include a different aldehyde with formation of mixtures of dioxolanes;[236] electron-deficient ketones such as isatins (Eq. 45) and quinones;[237,238] electron-deficient alkenes;[239,240] alkynes (Eq. 12);[88,241] imines;[195,197] and azodicarboxylates.[106] In some cases, catalyst-dependent diastereocontrol is observed, implicating the involvement of a catalyst-associated carbonyl ylide.[189]



(Eq. 45)

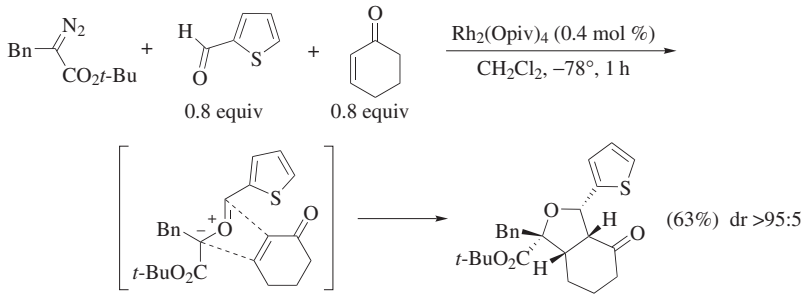
Use of a cobalt-cluster-modified alkynal as the dipole carbonyl source reverses and enhances diastereoselectivity compared with a simple alkynal, as well as

improving reaction efficiency and broadening the range of viable dipolarophiles (Eq. 46).[242]



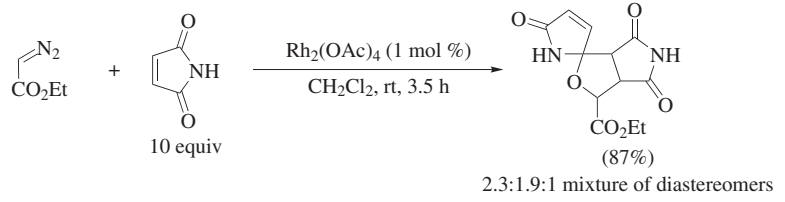
(Eq. 46)

The diazocarbonyl component is most often an α-diazoester; α-silylated and α-trifluoromethyl-substituted derivatives can exert good levels of stereocontrol (Eq. 11).[87,243] α-Alkyl-α-diazo esters are excellent substrates that react cleanly to give dioxolanes and functionalized dihydro- and tetrahydrofurans with high diastereocontrol at low temperature (Eq. 47).[106,244] A sterically demanding catalyst and a sterically demanding alkoxy group in the diazo ester are both important for good stereoselectivity and yield in cycloadditions using α-alkyl-α-diazo esters. The high reactivity of the ylide at low temperature in Eq. 47 may be attributed to the alkyl group raising the energy of the ylide MOs, relative to systems lacking the alkyl group, thereby reducing the $LUMO_{dipolarophile}-HOMO_{dipole}$ energy difference. The diastereoselectivity in cycloadditions using α-alkyl-α-diazo esters is unusal. The ester group and the aryl group from the aldehyde forming the ylide are *cis* in the cycloadducts, whereas these groups are generally *trans* in cycloadducts from α-diazo acetates, and α-aryl-, α-silylated-, and α-trifluoromethyl-substituted derivatives (Eqs. 11 and 44). Also, in the cycloadducts from α-alkyl-α-diazo esters, the substituents from the dipolarophile are *cis* to the ester group from the starting α-alkyl-α-diazo esters (Eq. 47), in contrast to Eq. 44. The diastereoselectivity with α-alkyl-α-diazo esters may be rationalized using the ylide and transition state shown in Eq. 47; however, the origin of this selectivity is unclear. Adjacent C–H insertion to give *cis*-α,β-unsaturated esters is a problematic competing reaction of the α-alkyl-α-diazo esters only when using electron-deficient catalysts.



(Eq. 47)

As already illustrated in Eqs. 11, 12, 44, 45, and 47, the carbonyl component forming an acyclic ylide is typically an aromatic aldehyde. This requirement avoids potential collapse of the ylide by a 1,4-hydrogen shift,[245] although examples using aliphatic aldehydes[235,243] (Eq. 1)[42] as well as ketones[246] also exist. Maleimide can provide both the carbonyl component for forming the ylide as well as the alkene dipolarophile to give the cycloadduct mixture shown in Eq. 48, along with traces of diethyl fumarate and maleate.[247,248] Slow addition of ethyl diazoacetate is used to avoid pyrazoline formation occurring from direct cycloaddition with maleimide.



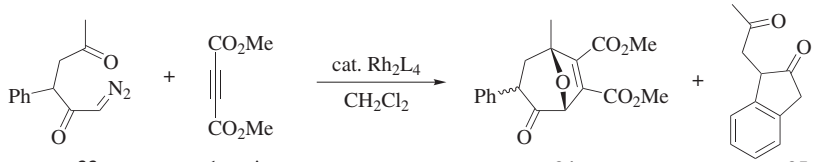
(Eq. 48)

Intermolecular generation of a carbonyl ylide, in which the carbonyl group forming the ylide and the dipolarophile are joined, followed by intramolecular cycloaddition is known, but rare (Eq. 1).[42]

Limitations and Side-Reactions

Limitations and side-reactions arise wherein efficient generation of the carbonyl ylide is compromised by alternative reactions of the initial rhodium metallocarbene, and where the carbonyl ylide intermediate undergoes transformations other than cycloaddition. Competing transformations of the rhodium metallocarbene include cyclopropanation and C–H insertion. Intramolecular versions of these processes can compete with carbonyl ylide formation where a favorable 1,5-relationship exists between the diazo carbon and the dipolarophile or a reactive C–H bond. Electronically disparate ligands in dimeric rhodium(II) catalysts influence carbene stabilization, thus influencing the competition between carbenoid processes.[60,64,65,119] For example, in Eq. 4 the ratio of ylide-derived cycloadducts/cyclopropanes is increased from 1:1 to 2:1 by moving from the relatively electron-deficient $Rh_2(tfa)_4$ catalyst to the comparatively electron-rich $Rh_2(cap)_4$-catalyst.[54] Catalyst influence on

product outcome is also seen in competition between intramolecular C–H insertion and carbonyl ylide formation–cycloaddition.[57,65] $Rh_2(OAc)_4$-catalyzed decomposition of diazo dione **33** in the presence of DMAD furnishes a mixture of oxabicyclooctene **34** and indanone **35** (Eq. 49).[249] However, only the carbonyl-ylide-derived cycloadduct **34** is produced on changing the catalyst to $Rh_2(cap)_4$. In contrast, use of the more electrophilic rhodium(II) perfluorobutyrate [$Rh_2(pfb)_4$] catalyst results in exclusive formation of the C–H insertion product **35**.

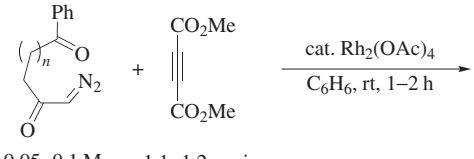


33 1 equiv **34** **35**

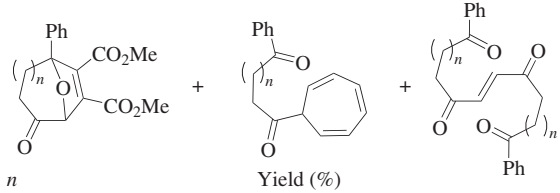
			Yield (%)	
Rh_2L_4	Temp	Time (h)	**34**	**35**
$Rh_2(OAc)_4$	—	—	60	20
$Rh_2(cap)_4$	45°	1	90	—
$Rh_2(pfb)_4$	rt	1	—	85

(Eq. 49)

As noted earlier ("Scope of the Carbonyl Group Forming the Ylide" section), five- to seven-membered-ring ylides have been generated in situ,[110,111] but efficiency generally diminishes with the larger rings.[112,113,113a] As indicated in Eq. 50, reaction with solvent and dimerization can become competitive.



0.05–0.1 M 1.1–1.2 equiv

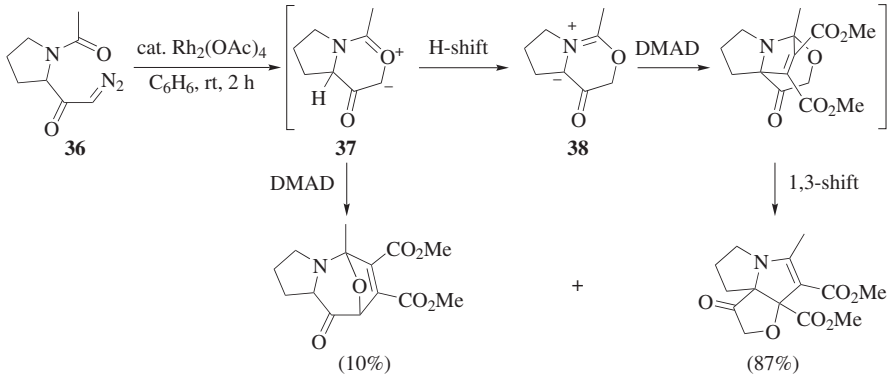


n		Yield (%)	
1	93	—	—
2	45	22	—
3	—	11	14

(Eq. 50)

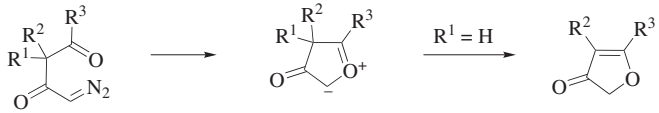
With certain diazocarbonyl substrates, products likely arising from the interconversion of one dipole into another can be observed.[223,227] For example, the reaction of diazo ketone **36** in the presence of $Rh_2(OAc)_4$ leads to products derived from azomethine ylide **38**. The process is suggested to proceed by isomerization (formal hydrogen shift) of an initially formed carbonyl ylide **37** to

the thermodynamically more stable azomethine ylide **38** (Eq. 51).[223,224] This process can be compared with the closely related substrate in Eq. 38, where normal carbonyl ylide formation-cycloaddition takes place as the benzyl substituent precludes a hydrogen shift.



(Eq. 51)

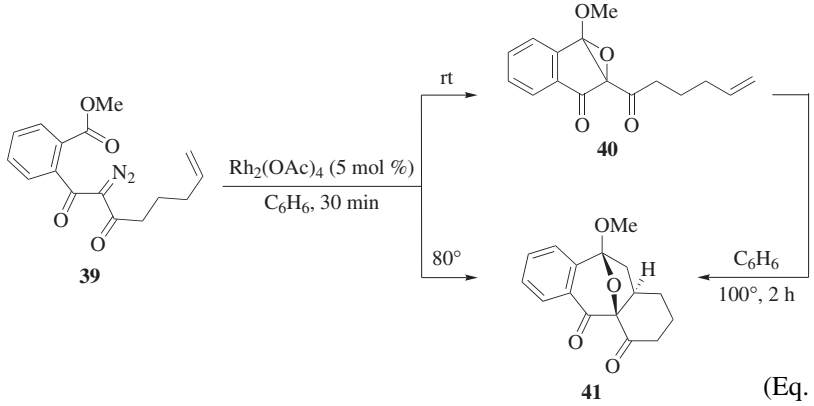
When the precursor for five-membered-ring ylide formation contains a stabilizing carbonyl group in the ylide ring (Eq. 52), it is preferable that R^1 and/or $R^2 \neq$ H to avoid the possibility of the intermediate ylide undergoing a 1,4-hydrogen shift to give an enol ether (furanone) faster than cycloaddition.[250] A deuterium labelling study of enol ether formation by way of intermolecular carbonyl ylide generation from ethyl diazoacetate and cyclohexanone indicates the hydrogen shift is intramolecular, which suggests the process is a suprafacial [1,4] sigmatropic rearrangement.[245] Such a rearrangement to give enol ethers and products derived from them can also occur with six-membered-ring ylides if the cycloaddition partners are poor dipolarophiles, such as 1-octene or cyclohexene,[45] or are absent.[251]



(Eq. 52)

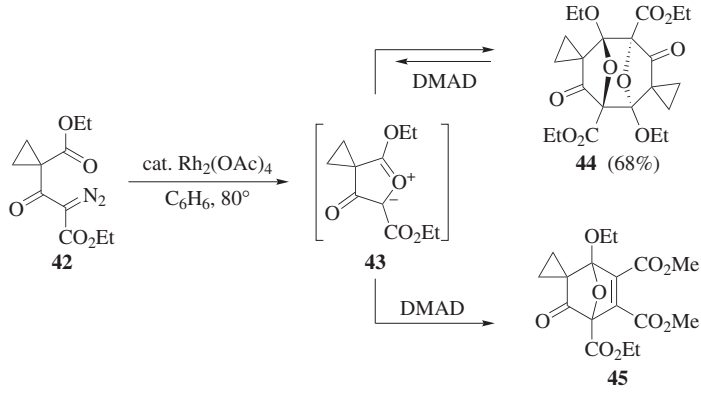
Carbonyl ylides derived from certain diazo and carbonyl compounds, in the absence of suitable dipolarophiles, can undergo electrocyclic ring closure. The process is typically seen with stabilized acyclic ylides from aryl-, heteroaryl-, and vinyl-substituted diazoacetates with α,β-unsaturated aldehydes or ketones. Electrocyclic ring closure results in epoxides,[252–254] dihydrofurans,[255] or dioxolenes from 2-diazo-1,3-diones or diazoacetoacetates via cyclization through the ketonic oxygen.[256–258] One interesting example is shown in Eq. 53, where reaction of diazodione **39** at ambient temperature leads to isolation of the epoxide **40** and traces of cycloadduct **41**, whereas at 80° cycloadduct **41** is formed exclusively.[205,206] Epoxide **40** is converted into product **41** at 100° in the absence

of a catalyst. The presence of the methoxy group in epoxide **40** likely provides a reaction pathway to and from the intermediate carbonyl ylide, which overrides the geometric constraints of conrotatory electrocyclic ring-opening or -closing, respectively.



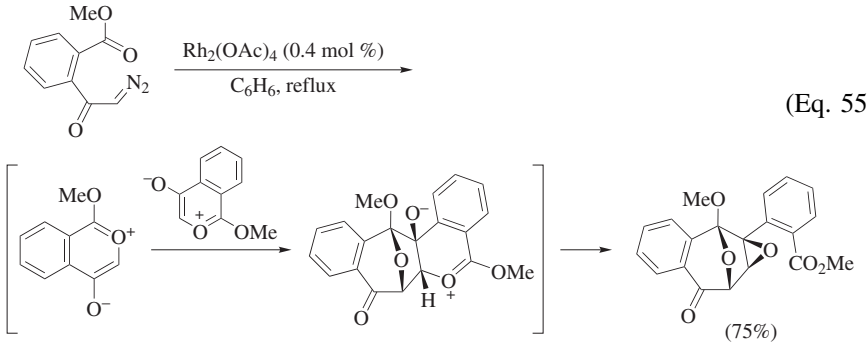
(Eq. 53)

Reaction of diazo ester **42** under $Rh_2(OAc)_4$ catalysis in the absence of a dipolarophile likely proceeds via ylide **43**, which undergoes dimerization to produce the head-to-tail dimer **44** (Eq. 54).[155,157] Isomerization to the corresponding epoxycyclobutanone may be disfavored due to strain, although such a process has been claimed.[142] Heating of the dimer **44** with the reactive dipolarophiles DMAD (or *N*-phenylmaleimide) in the absence of a catalyst, leads to cycloadduct **45** likely derived from the ylide **43**.



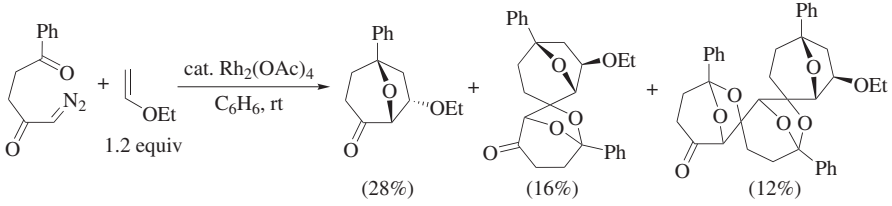
(Eq. 54)

An alternative dimerization pathway open to a more stable (aromatic) carbonyl ylide in the absence of a dipolarophile (or in the presence of an unreactive or unactivated dipolarophile) is shown in Eq. 55.[44,259] The formation of dimers (Eqs. 54 and 55) suggest that in these cases the carbonyl ylides accumulate in the reaction or that they can be reversibly accessed from the corresponding epoxyketone isomers (Eq. 53).[103,104]



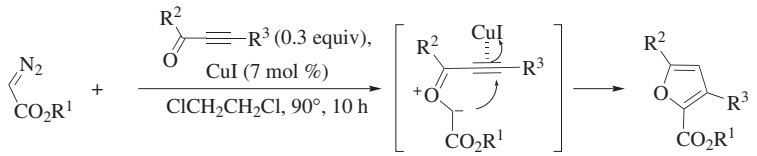
(Eq. 55)

If the dipolarophile reacts slowly, due to an inherent mismatch and/or is not used in sufficient excess with the particular ylide generated, then, as the cycloadduct forms, the keto functionality within it can start to act as a competitive dipolarophile, resulting in mixtures of higher cycloadducts (Eq. 56).[45]



(Eq. 56)

Formal copper(I)-catalyzed [4 + 1] cycloaddition of diazoacetates with α,β-unsaturated ketones and α,β-acetylenic ketones gives 2,3-dihydrofurans[260] and furans,[261] respectively. This reaction has been suggested to proceed by way of intermolecular carbonyl ylide formation, followed in the latter case (Eq. 57) by ring closure onto the triple bond and proton transfer.



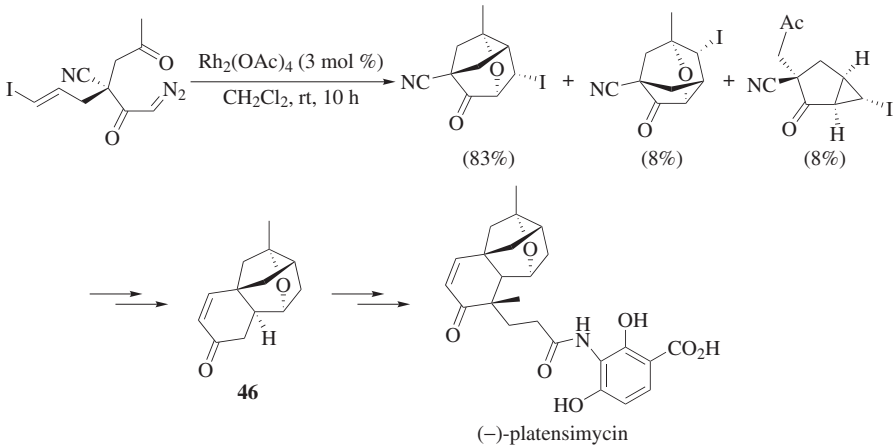
(Eq. 57)

APPLICATIONS TO SYNTHESIS

The power of tandem carbonyl ylide formation–cycloaddition using diazocarbonyl compounds has been amply demonstrated in diverse strategies toward a range of structurally and biologically interesting natural and unnatural targets.[19,26]

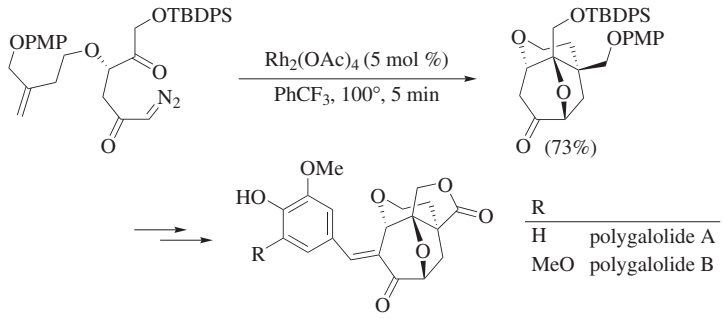
Intramolecular Cycloadditions

A formal asymmetric synthesis of the antibiotic platensimycin has been accomplished by the synthesis of tetracyclic enone **46** (Scheme 9).[55] In the key step, the temporary presence of the terminal halogen substituent on the tethered alkene dipolarophile is necessary to favor the desired cycloaddition regioselectivity.



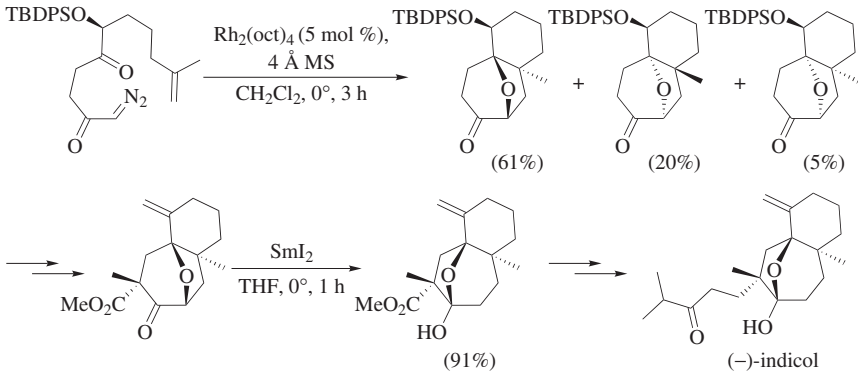
Scheme 9

Intramolecular cycloaddition of a diazo ketone gives a dioxatricyclic ring system, which is subsequently elaborated into polygalolides A and B by lactone construction and a Mukaiyama aldol-type reaction (Scheme 10).[67,261a] In this case, the cycloaddition is completely regioselective as the alternative constitutional isomer would have to form by way of a considerably more sterically encumbered transition state. The authors speculate that the polygalolides are biosynthesized by a strategically related intermolecular oxidopyrylium cycloaddition (Scheme 25 in "Comparison with Other Methods" section).



Scheme 10

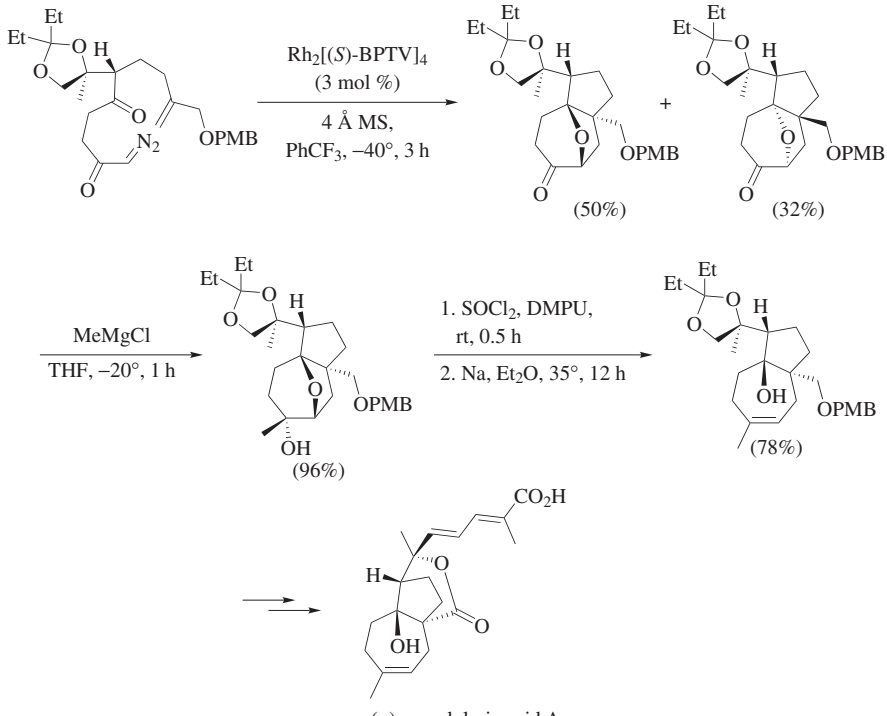
The synthesis of the antifeedent secodolastane (−)-indicol illustrates the ability of a stereocenter in the tethered dipolarophile to influence diastereofacial selectivity (Scheme 11).[76] The formation of the desired major diastereomer proceeds through a transition state in which the tether adopts a chair conformation, with the bulky silyloxy group residing in an equatorial position. The diastereofacial selectivity could not be improved using a matched chiral catalyst. No degradation of enantiopurity is observed at the potentially enolizable stereocenter during the cycloaddition process. Although the cycloaddition installs the oxygen bridge, treatment with SmI_2 produces the desired hemiacetal.



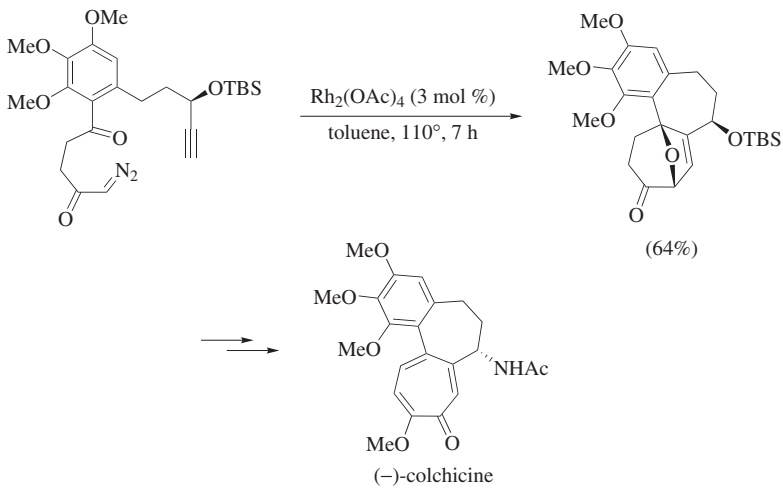
Scheme 11

A similar key step is used in the synthesis of the diterpenoid pseudolaric acid A (Eq. 15, Scheme 12).[74] In this case, the use of the achiral catalyst $Rh_2(OAc)_4$ favors the undesired cycloadduct in a ratio of 3:1. However, use of the chiral catalyst $Rh_2[(S)\text{-BPTV})]_4$ reverses the inherent substrate bias. The likely slower rate of cycloaddition of the hexenyl-tethered substrate[43] in the indicol synthesis (Scheme 11), compared with that of the pentenyl-tethered one in the pseudolaric acid A synthesis, may lead to cycloaddition taking place from a fully catalyst-dissociated ylide in the former system, thus explaining the divergent dependence on catalyst structure.

Approaches to the tigliane diterpenes have examined the influence of stereocenters within the ylide-forming ring,[117] as well as that of a cyclopropane in the tethered dipolarophile.[78] An asymmetric synthesis of (−)-colchicine is notable for the scale of the cycloaddition event (5 g, 10 mmol), as well as the seven-membered-ring closure, albeit in a restricted system, and for the complete diastereocontrol induced by the propargylic stereocenter in the tethered dipolarophile (Scheme 13).[82,261b] Slow syringe-pump addition of the substrate to a vigorously stirred suspension of the catalyst in refluxing toluene is essential for successful cycloaddition. Standard reaction conditions, in benzene at room temperature, lead only to a dihydropyranone due to a 1,4-hydrogen shift from the intermediate carbonyl ylide (see also Eq. 52).

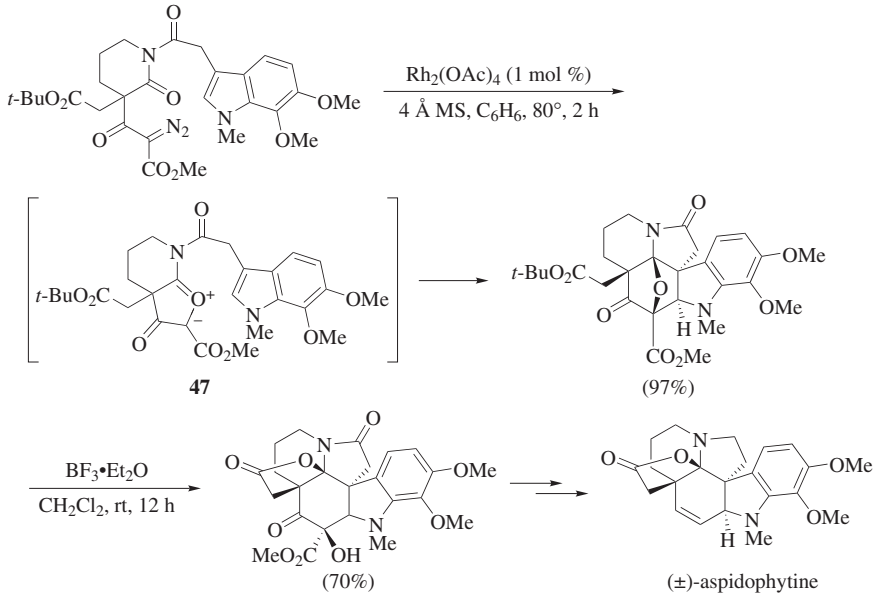


Scheme 12



Scheme 13

Intramolecular cycloadditions of ester-derived oxidopyrylium ylides are used in the synthesis of benzo-fused analogues of tropolone natural products,[125] in studies toward the alkaloid ribasine,[119] and toward the trypanocidal diterpene komaroviquinone.[206] Intramolecular cycloadditions of non-aromatic five-membered-ring carbonyl ylides from imides, with the dipolarophile being a tethered indole, are used for accessing the *aspidosperma* alkaloids, including a total synthesis of (±)-aspidophytine (Scheme 14),[139,141] an enantioselective approach,[142] and toward the kopsifoline alkaloids.[215]

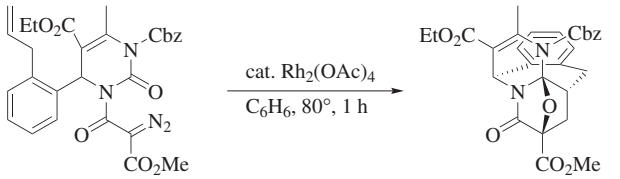


Scheme 14

The cycloadduct configuration reported in the synthesis of (±)-aspidophytine is unusual (Scheme 14) because it implies the tethered indole undergoes cycloaddition through a strained *exo*-transition state. It is argued that the sterically demanding *tert*-butyl ester influences the cycloaddition to occur on the opposite face of the intermediate ylide **47** to which it is attached, as well as orienting the tethered indole *exo*. However, the subsequent transformations, in which the ether bridge and its configuration are lost, do not definitively rule out a more normal *endo*-selective cycloaddition occurring on the same side as the *tert*-butyl ester (see also Scheme 24 in "Comparison with Other Methods" section).

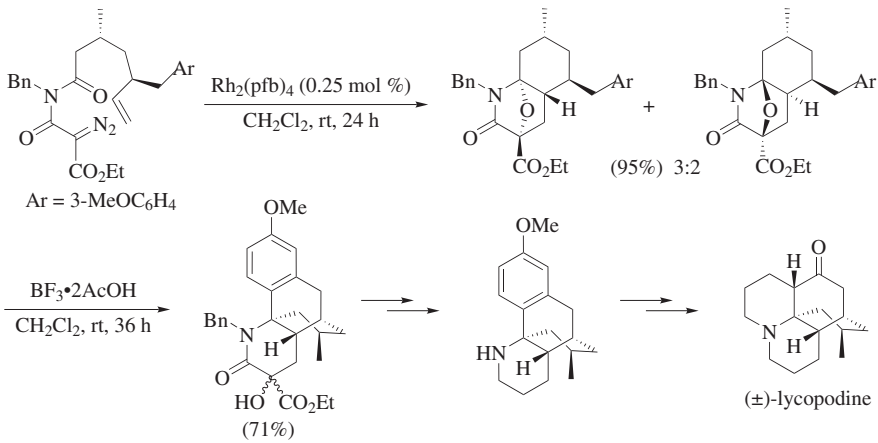
Intramolecular cycloadditions proceeding through isomünchnone intermediates have been applied to several targets. For example, such reactions form the basis of an ultimately unsuccessful approach to lysergic acid,[129] a formal synthesis of the indoline (±)-vallesamidine,[212] and a diversity-oriented synthesis of indole alkaloid-like skeletons.[136] Conformationally rigid polyheterocycles that mimic the putative receptor-bound conformation of dihydropyrimidine-type calcium channel

modulators are obtained through completely regioselective cycloaddition of a dihydropyrimidine-fused isomünchnone (Eq. 58).[62] Structurally related acyclic ureas cyclize preferentially to ammonium ylides, and Cbz-protection at nitrogen is necessary to avoid collapse of the isomünchnone by a [1,5] hydrogen shift.



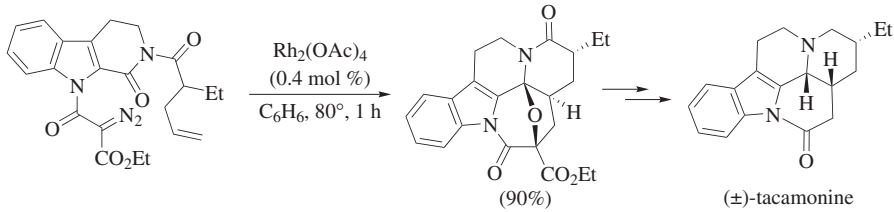
(Eq. 58)

An intramolecular isomünchnone cycloaddition is used in a formal synthesis of the alkaloid (±)-lycopodine (Scheme 15).[73] Cycloaddition occurs exclusively in an *exo* fashion where the tether ends up *syn* to the ether bridge as expected, but with poor diastereoselectivity with respect to the preexisting stereocenters in the tether. Interestingly, in the absence of the methyl group, a single diastereomer, with the 3-methoxybenzyl group and ether bridge *anti*, is isolated in 95% yield. However, the poor diastereoselectivity is of no major consequence in the context of the lycopodine synthesis. In the subsequent BF_3•2AcOH-complex-induced cyclization, the undesired methine configuration is inverted during *N*-acyl iminium ion–enamide interconversion and the resulting epimeric mixture of tertiary alcohols then undergoes radical deoxygenation and decarboxylation.



Scheme 15

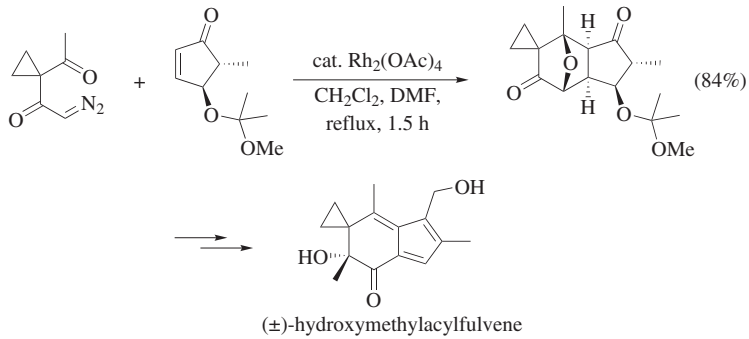
Cyclization via six-membered-ring imide-derived carbonyl ylides and a base-induced keto amide ring-contraction process are used in syntheses of the *vinca* alkaloid (±)-3*H*-epivincamine and, through a common cycloadduct, the *tacaman* alkaloids (±)-tacamonine (Scheme 16) and (±)-apotacamine.[80] The tethered dipolarophile undergoes *exo*-cycloaddition with complete selectivity for one face of the carbonyl ylide under the control of the ethyl-bearing stereocenter.



Scheme 16

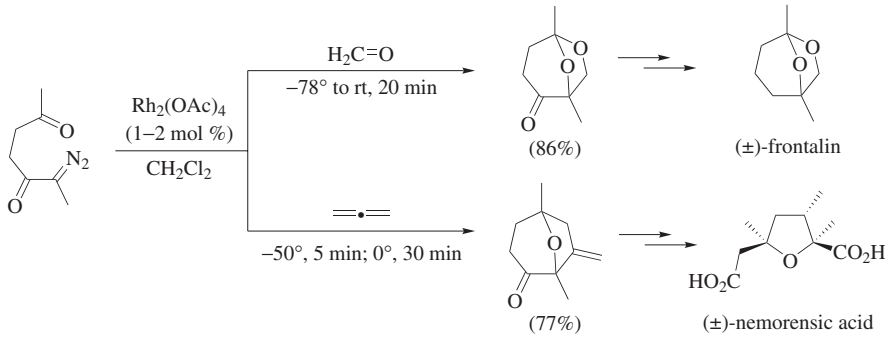
Intermolecular Cycloadditions

The five-membered-ring carbonyl ylide derived from 1-acetyl-1-(diazoacetyl) cyclopropane has been employed in intermolecular cycloadditions with a wide range of dipolarophiles, even undergoing cycloaddition with the comparatively non-activated cyclopentene.[58] With cyclopentenones, this construction has led to the syntheses of several biologically active sesquiterpenoids, including the illudins[79,156,177,262,263] and their derived antitumor acylfulvenes,[173–175] and pterosins.[58] In a synthesis of the hydroxymethylacylfulvene antitumor agent shown in Scheme 17,[174] a single diastereomer is formed in the cycloaddition. Although the *exo*-selectivity is as expected, the complete face selectivity seen with the dipolarophile is notable and is attributed to a steric interaction that could arise between the ylide and the α′-methyl of the cyclopentenone in the alternative *exo* transition state.



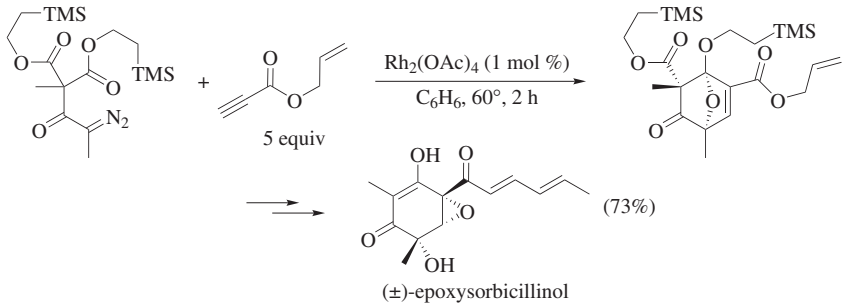
Scheme 17

Brevicomin syntheses represent an early application of an intermolecular cycloaddition of a ketone-derived six-membered-ring carbonyl ylide, using 1-diazohexane-2,5-dione with propanal as the dipolarophile.[45,191] A related strategy, using the diazodione in Scheme 18 with formaldehyde as the dipolarophile, results in a formal synthesis of frontalin.[105] Scheme 18 also provides an example of allene as a dipolarophile in a regioselective cycloaddition, which leads to various nemorensic acids following oxidative cleavage of the ketone-derived silyl enol ether.[105,264,265]



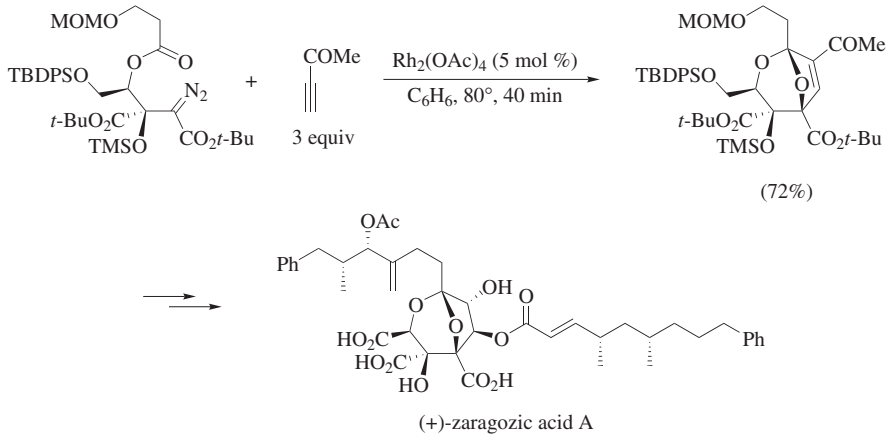
Scheme 18

Intermolecular cycloaddition of an achiral ester-derived five-membered-ring carbonyl ylide is used in a synthesis of the vertinoid polyketide (±)-epoxysorbicillinol (Scheme 19).[186]



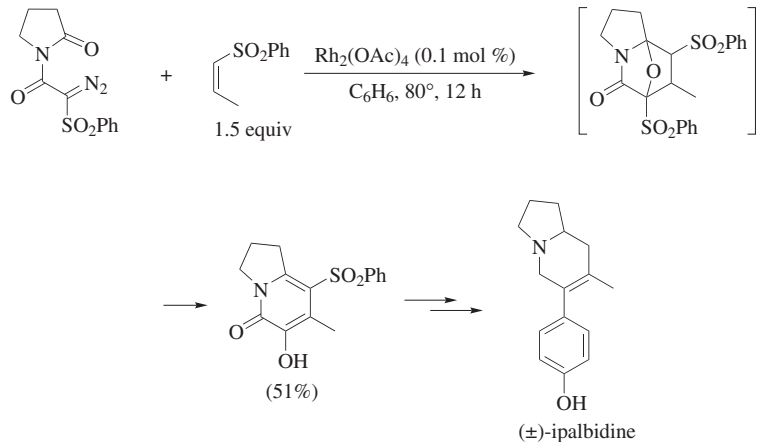
Scheme 19

Methyl glyoxylate serves as the dipolarophile in an approach to the 2,8-dioxabicyclo[3.2.1]octane core of the squalene synthase inhibitors zaragozic acids, which involves subsequent acid-catalyzed rearrangement of the initially formed 6,8-dioxabicyclo[3.2.1]octane cycloadduct (Eq. 10).[83,84] Total syntheses of zaragozic acids A and C involve a detailed study of an intermolecular cycloaddition of an ester-derived six-membered non-aromatic carbonyl ylide.[47,266] The conditions shown in Scheme 20 involving an acetylenic ketone as the dipolarophile are optimal for the target syntheses, although other catalysts/conditions and dipolarophiles with different ester groups on the tartrate-derived dipole were also examined. The product profile is acutely sensitive to the reaction temperature. Under otherwise identical reaction conditions to those shown in Scheme 20, but at 60°, only 7% of the desired cycloadduct is observed, with the major product (65%) arising from formal addition of water to the diazo-bearing carbon.



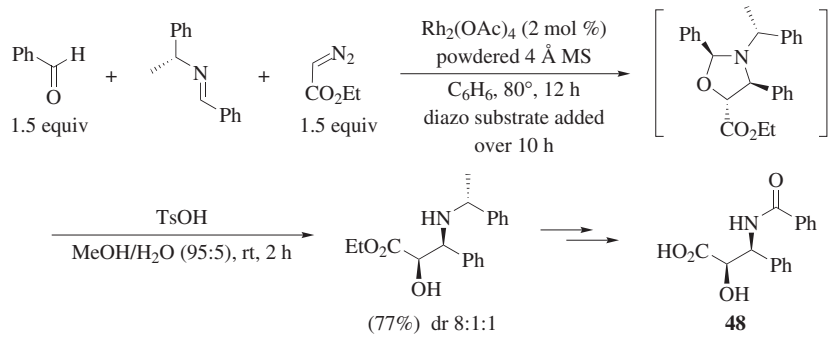
Scheme 20

A sulfone-substituted, diazo imide-derived isomünchnone is used in intermolecular cycloadditions to generate 2-pyridones, following loss of benzenesulfinic acid under the reaction conditions (Scheme 21).[154,159,267] The method was applied in the syntheses of several indolizidine alkaloids, such as (±)-ipalbidine, and the angiotensin-converting enzyme inhibitor (−)-A58365A.



Scheme 21

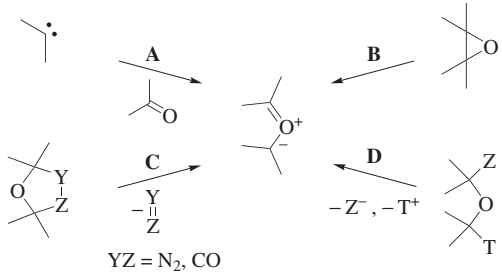
A chiral-auxiliary-bearing imine is used as the dipolarophile in a three component carbonyl ylide cycloaddition to give, following hydrolysis of the intermediate oxazolidine cycloadduct, the *syn* β-amino alcohol in 77% yield (Scheme 22).[195,197] Hydrogenolysis, followed by benzoylation and saponification gives the paclitaxel side chain **48**.



Scheme 22

COMPARISON WITH OTHER METHODS

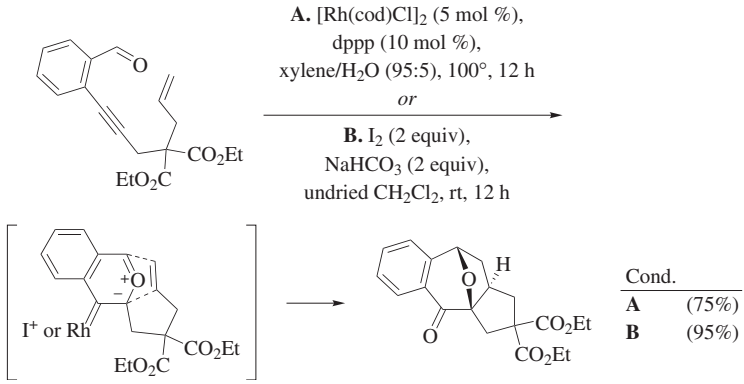
Although many methods are available for generating carbonyl ylides for use in cycloadditions,[12,15] interception of diazocarbonyl compounds is by far the most widely employed. The popularity of this approach stems in part from the ready availability and reasonable stability of structurally diverse α-diazocarbonyl compounds, combined with mild conditions for the subsequent generation of the carbonyl ylide and wide scope with respect to the type of carbonyl ylide generated, particularly in non-aromatic systems, and the dipolarophile partner. The generation of carbonyl ylides can generally be classified into four strategies (Scheme 23): (1) trapping of carbenes or carbene equivalents with carbonyl compounds (**A**); (2) electrocyclic ring-opening of epoxides (**B**); (3) cycloreversions (**C**); and, (4) eliminations (**D**). Each of these strategies, and the main methods which comprise them, are discussed in turn below.



Scheme 23

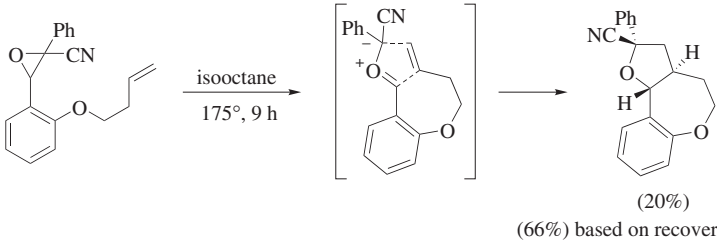
The strategy of carbonyl ylide generation–cycloaddition by initial trapping of carbenes or carbene equivalents using carbonyl compounds is dominated by the α-diazocarbonyl chemistry discussed in this chapter. The use of an alkyne as an alternative formal carbene source is an emerging method.[268,269] In the examples shown in Eq. 58,[270,271] hydration of an intermediate metal- or iodide-stabilized carbocation is proposed to lead to the final keto group, although in other cases

this species can undergo more complex transformations.[272] These alkyne-derived carbonyl ylides appear to be limited to aromatic species.[273]



(Eq. 58)

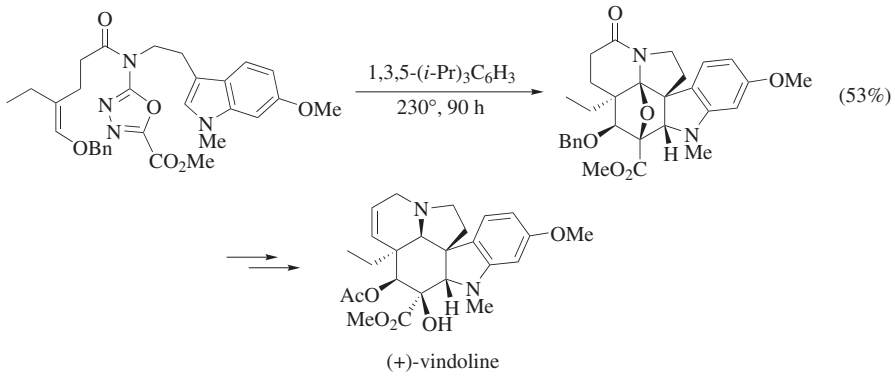
Thermolysis or photolysis of epoxides typically possessing electron-withdrawing and/or conjugating substituents can generate carbonyl ylides which undergo dipolar cycloadditions (Eqs. 53, 59).[274–276b]



(Eq. 59)

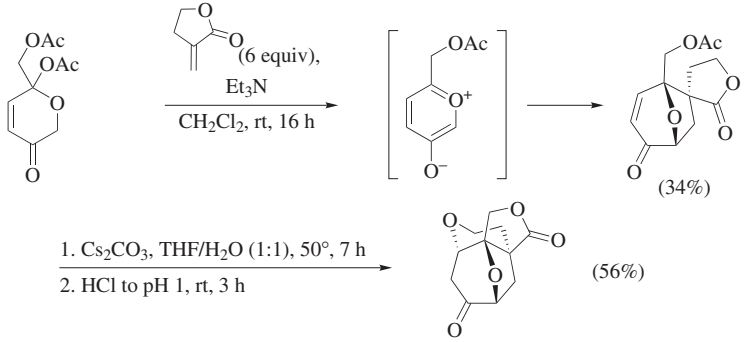
Thermal extrusion of nitrogen by retro 1,3-dipolar cycloaddition from 1,3,4-oxadiazolines provides carbonyl ylides (Scheme 23, YZ = N_2). As part of a tandem [4 + 2]/[3 + 2] cycloaddition approach to *aspidosperma* alkaloids, a 1,3,4-oxadiazoline is generated from an inverse-electron-demand [4+2] cycloaddition of a 1,3,4-oxadiazole (Scheme 24).[277,278,278a] The carbonyl ylide cycloaddition onto the tethered indole in this sequence can be compared with the related α-diazocarbonyl-derived process shown in Scheme 14. In Scheme 24 a single diastereomer is generated from exclusive *endo* mode indole [3+2] cycloaddition with the carbonyl ylide on the face opposite to the newly formed lactam.

Diverse and useful elimination processes exist for the generation of carbonyl ylides, especially for aromatic and non-stabilized systems. These methods can provide carbonyl ylides not accessible using α-diazocarbonyls. Base- and/or heat-induced elimination from (often furan-derived) pyranulose acetates is a popular method for generating oxidopyrylium ylides.[279,280] Scheme 25 shows a biomimetically inspired approach to the tricyclic framework of polygalolides A and B



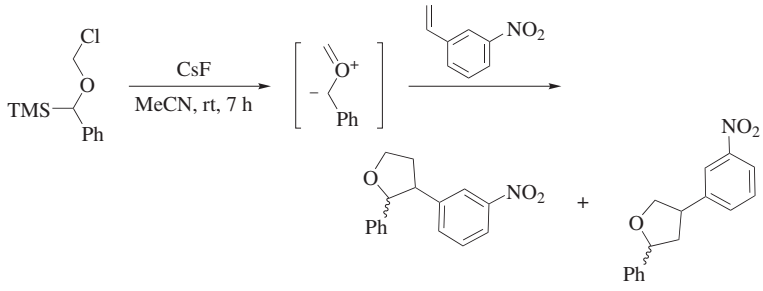
Scheme 24

using a pyranulose acetate-derived intermolecular oxidopyrylium cycloaddition, followed by hydrolysis of the cycloadduct.[281] Although racemic, this approach is more concise than a previous α-diazo ketone-intramolecular-cycloaddition based synthesis of polygalolides A and B (Scheme 10).

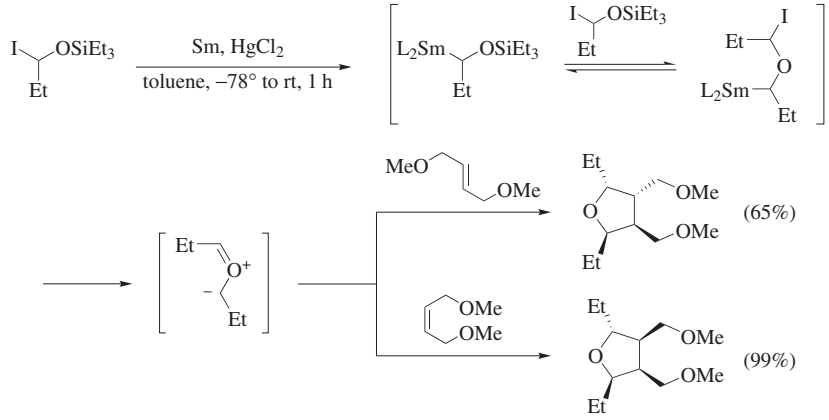


Scheme 25

Nonstabilized carbonyl ylides, which undergo cycloadditions with a range of dipolarophiles, can be generated by several 1,3-elimination methods. Fluoride-induced desilylation of chloromethyl silylmethyl ethers provide aryl-substituted carbonyl ylides (Eq. 60).[282] Samarium(0)- or Mn/Pb-induced reduction of aldehyde/TMSI-derived iodomethyl silyl ethers provide alkyl-substituted carbonyl ylides.[283,283a] Eq. 61 indicates that a pericyclic process is operative and, furthermore, suggests that these reactions proceed by way of a sickle-shaped carbonyl ylide (see also Eq. 44). Generation of the parent unsubstituted carbonyl ylide for cycloadditions is best achieved by Mn/Pb-induced 1,3-elimination from bis(chloromethylether).[283b]



(Eq. 60)



(Eq. 61)

EXPERIMENTAL CONDITIONS

Availability of α-Diazocarbonyl Substrates

Methods for the synthesis of the types of α-diazo carbonyl compounds used in carbonyl ylide cycloadditions have been extensively reviewed[5,10,284] and are also summarized in a recent *Organic Reactions* chapter.[285] The four principal methods comprise: (1) reaction of activated carboxylic acid derivatives with diazoalkanes (see Eq. 16);[286] (2) diazo transfer reactions using arylsulfonyl azides that are particularly suitable for compounds containing an additional electron-withdrawing group or unsaturation at the β-position, or ultimately a single carbonyl group where a β-formyl group is lost during diazo transfer; (3) thermolysis of tosylhydrazones (useful for alkyl diazoacetates);[287] (4) functionalization/elaboration of a diazocarbonyl derivative. With reference to the fourth method, a number of transformations, including cross-metathesis,[122] can be carried out on substrates bearing a pre-existing diazocarbonyl functionality, especially with substrates further stabilized by an additional electron-withdrawing group at the β-position. A SciFinder search in 2011 indicated approximately 300 commercially available α-diazocarbonyl compounds.

General Reaction Conditions

A variety of catalysts (Charts 1 and 2 at the beginning of the "Tabular Survey") have been used with diazocarbonyl groups in carbonyl ylide cycloadditions. Although copper-, ruthenium-, and palladium-based catalysts have been examined, by far the most popular are rhodium-based, especially $Rh_2(OAc)_4$. Structurally related dirhodium catalysts are typically derived by ligand exchange. Variation of the bridging carboxylate or carboxamide ligands provides some scope with respect to control over catalyst solubility, reactivity, and selectivity (Eqs. 4 and 49), especially chiral ligands (Chart 2) for enantioselective cycloadditions. Rhodium(II) octanoate possesses good solubility in nonpolar solvents, rhodium(II) trifluoroacetate has high electrophilicity, whereas rhodium(II) carboxamidates and carboxamides (for example, rhodium(II) caprolactamate) are comparatively less reactive electron-rich catalysts. Most of the catalysts are stable compounds, or can be generated in situ from stable precursors. A ruthenium porphyrin catalyst supported on poly(ethylene glycol) (Chart 1) has been used with 1-diazo-2,5-hexanedione and DMAD in a tandem intramolecular carbonyl ylide formation–intermolecular cycloaddition reaction.[171] The catalyst is recovered by filtration and, following drying, is re-used in six otherwise identical consecutive reaction runs without apparent loss of catalytic activity (over 5700 product turnovers).

Catalyst loading is typically in the range 0.2–5 mol %, and the catalyst is normally added in one portion. For intermolecular processes, the diazo compound is often added slowly to a stirred solution of the catalyst and the dipolarophile. An excess of dipolarophile is usually used to minimize side-reactions such as water addition, dimerization, or insertion. Good yields of cycloadducts can be obtained with just one equivalent of dipolarophile, provided syringe-pump techniques are used for addition of the diazocarbonyl compound. Reactions are typically carried out in an inert atmosphere under anhydrous conditions; the presence of 4 Å molecular sieves may be beneficial in some cases (Scheme 11).[76,134]

Solvents can have a significant influence on the efficiency, and diastereo- and enantioselectivity of cycloadditions.[46,76,85,182] Popular solvents are CH_2Cl_2 or benzene, but many other solvents have also been used, such as 1,2-dichloroethane, fluorobenzene, toluene, hexane, pentane, or diethyl ether. Cycloadditions have been shown to occur with improved yields in ionic liquids.[190] The high solubility of $Rh_2(OAc)_4$ in the ionic liquid compared with the subsequent ethyl acetate–hexane solvent mixture used for extracting the cycloadduct also allows efficient re-use of the catalyst and ionic liquid. Four further cycles were demonstrated without any reduction in cycloadduct yield. The presence of 10% DMF in CH_2Cl_2 improves yields in an intermolecular cycloaddition (Scheme 17).[177] It is suggested that the DMF binds reversibly to the $Rh_2(OAc)_4$ resulting in slower carbenoid formation. The decreased carbenoid concentration limits competing side reactions, such as dimerization. Reactions are often run at ambient temperature or at reflux in CH_2Cl_2 or benzene. With the less reactive diazomalonates and diazoacetoacetates, higher reaction temperatures are often required. Chemo-, regio-, and stereoselectivity can show marked temperature effects (Scheme 20).[47]

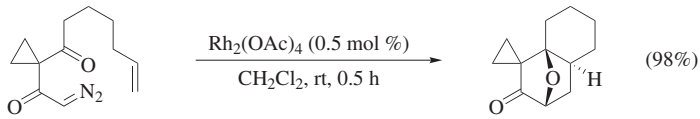
Reaction efficiency has been improved by using a microwave reactor[134,288] and in a continuous flow system using an immobilized chiral rhodium(II) catalyst.[288a]

Safety Considerations

The frequently used solvent benzene is a suspected carcinogen. Tosyl azide, the standard reagent for diazo-transfer reactions, has the explosive power of TNT; safer alternatives are available.[289] *Great care should be taken in handling diazocarbonyl compounds because they are potentially toxic and can have explosive properties. Even though diazocarbonyl compounds containing electron-withdrawing functionality are much more stable than their diazoalkane counterparts, detailed studies on the potential dangers of many of the diazocompounds described in this review are not available. Therefore, diazocarbonyl compounds should be handled carefully and all reactions should be carried out in a well-vented fume hood, behind a blast shield.*

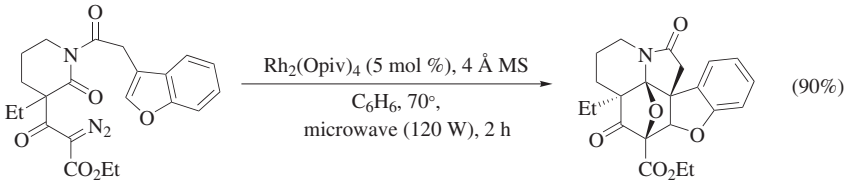
EXPERIMENTAL PROCEDURES

The examples in this section have been selected to illustrate a range of cycloaddition protocols, rather than substrate types. One of the advantages of cycloaddition reactions of carbonyl ylides derived from diazo compounds is that, in general, they are relatively straightforward to carry out. However, choice of catalyst (together with potential inclusion of a Lewis acid and/or a drying agent), solvent, reaction temperature, and, often for intermolecular reactions, order and rate of substrate addition are important practical considerations. To enable a judicious choice of initial reaction conditions to examine in a new reaction, the tables should be consulted for references to specific procedures on structurally related substrates.

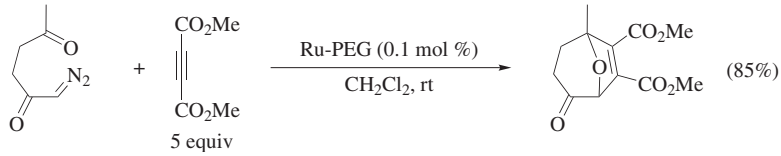


(98%)

Spiro[6,8a-epoxy-7-oxooctahydronaphthalene-8,1′-cyclopropane] [Intramolecular Cycloaddition of a Cyclic Carbonyl Ylide from an Unsaturated Ketone].[58] $Rh_2(OAc)_4$ (2 mg, 0.004 mmol) was added to a stirred solution of the unsaturated ketone (150 mg, 0.68 mmol) in CH_2Cl_2 (5 mL) at rt. After 30 min, the reaction mixture was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2, EtOAc/hexane) to give the cycloadduct as a clear oil (125 mg, 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.65 (m, 1H), 0.9–1.4 (m, 6H), 1.5–2.2 (m, 8H), 4.50 (d, $J = 6.3$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3, 12.3, 21.4, 25.0, 26.7, 32.5, 34.8, 37.3, 39.4, 80.4, 84.2, 213.6.

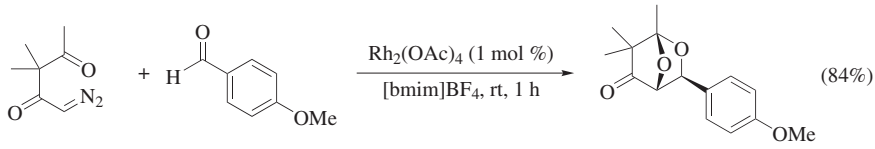


Ethyl 3a-Ethyl-5,12b-epoxy-4,12-dioxo-2,3,3a,5,5a,11,12,12b-octahydro-1*H*,4*H*-6-oxa-12a-azaindeno[7,1-*cd*]fluorene-5-carboxylate [Intramolecular Cycloaddition of a Cyclic Carbonyl Ylide from an Imide under Microwave Conditions].[134] $Rh_2(Opiv)_4$ (4 mg, 0.007 mmol) and 4 Å MS (1 g) were heated in a 10-mL microwave reactor container at 100° for 10 min under argon. A solution of the diazo imide (0.05 g, 0.117 mmol) in benzene (4 mL) was syringed into the container and the mixture was heated in the microwave apparatus at 70° (120 W) for 2 h. The mixture was then filtered through a pad of Celite, concentrated under reduced pressure, and purified by column chromatography (SiO_2, 10% EtOAc/hexane) to give the cycloadduct as a white solid (0.045 g, 90%): mp 185–187°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24–0.34 (m, 1H), 0.78 (t, $J = 7.2$ Hz, 3H), 0.83–0.91 (m, 1H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.52–2.12 (m, 4H), 2.86 (d, $J = 17.6$ Hz, 1H), 3.10 (d, $J = 17.6$ Hz, 1H), 3.22 (dt, $J =$ 12.8 and 4.4 Hz, 1H), 3.91 (dt, $J = 13.2$ and 5.6 Hz, 1H), 4.36–4.50 (m, 2H), 5.39 (s, 1H), 6.86–6.96 (m, 2H), 7.04–7.08 (m, 1H), 7.21–7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.1, 14.4, 17.9, 20.4, 24.8, 39.3, 43.4, 52.1, 59.3, 63.0, 90.1, 92.3, 104.8, 111.6, 122.2, 124.4, 126.3, 131.0, 160.7, 165.0, 176.4, 204.6.

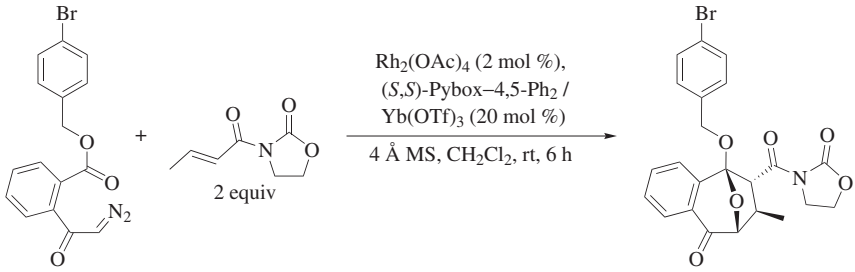


6,7-Dicarbomethoxy-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-2-one [Intermolecular Cycloaddition of a Cyclic Carbonyl Ylide from a Ketone with Catalyst Recovery].[171] A solution of the ketone (210 mg, 1.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise via a syringe pump over 30 h to a solution of DMAD (1 g, 7.5 mmol) and Ru–PEG (see Chart 1) (11 mg, 0.0015 mmol) in CH_2Cl_2 (10 mL) at rt. After the diazodione was completely consumed, the reaction mixture was evaporated under reduced pressure, dry Et_2O was added, and the solution cooled to 0° for 1 h. The polymer-supported catalyst was recovered for re-use by rapid filtration and washing with cold Et_2O (2 × 5 mL), followed by drying under reduced pressure. The filtrate (containing none of the catalyst, as determined by UV–visible spectrophotometry) was evaporated under reduced pressure and purified by column chromatography (SiO_2, 20% EtOAc/hexane) to give the cycloadduct as colorless crystals (324 mg, 85%): mp 62–64°; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3H), 2.23–2.28 (m, 2H), 2.50 (dddd, $J = 18.0$,

6.3, 3.0, 1.5 Hz, 1H), 2.77 (dt, $J = 18.0$, 8.7 Hz, 1H), 3.79 (s, 3H), 3.89 (s, 3H), and 4.83 (d, $J = 1.5$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 32.7, 32.9, 52.6, 52.7, 86.0, 88.3, 135.8, 147.0, 161.2, 163.9, 199.3.

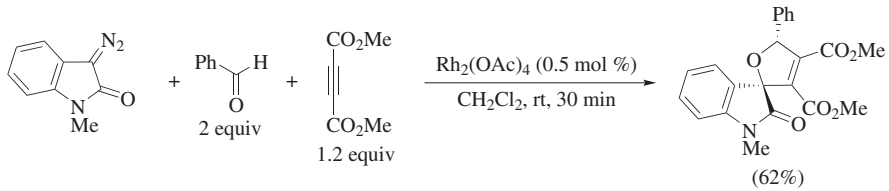


3-(4-Methoxyphenyl)-1,6,6-trimethyl-2,7-dioxabicyclo[2.2.1]heptan-5-one [Intermolecular Cycloaddition of a Cyclic Carbonyl Ylide from a Ketone in an Ionic Liquid with Solvent and Catalyst Recovery].[190] A mixture of the ketone (0.15 g, 1.0 mmol) and 4-methoxybenzaldehyde (0.14 g, 1.2 mmol) in well-dried 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (3 mL) was stirred for 5 min at rt to give a clear oily solution. $Rh_2(OAc)_4$ (4.3 mg, 0.01 mmol) was then added to the reaction mixture. After 1 h, the reaction mixture was extracted repeatedly (50% EtOAc/hexane, 5 × 10 mL) until the absence of any organic compound in the ionic liquid layer (the pale-yellow ionic liquid containing the catalyst was dried by heating to 100° under reduced pressure for 7 h to give 99% recovery for re-use). The combined organic solvent extracts were evaporated under reduced pressure and purified by column chromatography (15% EtOAc/hexane) to give the cycloadduct as a white solid (0.21 g, 84%): mp 75–77° ($CHCl_3$/hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.16 (s, 3H), 1.70 (s, 3H), 3.79 (s, 3H), 4.42 (s, 1H), 4.75 (s, 1H), 6.88 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.2, 19.5, 21.2, 53.0, 55.8, 77.6, 86.6, 114.5, 114.7, 128.2, 131.7, 160.3, 214.2.



5-(4-Bromobenzyl)oxy-7-*exo*-methyl-6-*endo*-(2-oxazolidinoyl)carbonyl-8-oxabenzo[*c*]bicyclo[3.2.1]octan-2-one [Asymmetric Intermolecular Cycloaddition of a Diazoketoester-Derived Pyrylium].[102] A solution of 2,6-bis[(4*S*, 5*S*)-(−)-4,5-diphenyl-2-oxazolin-2-yl]pyridine (52 mg, 0.10 mmol) in THF (3 mL) was added to a stirred solution of $Yb(OTf)_3$ (62 mg, 0.10 mmol) in THF (2 mL) at rt. After 2 h, the solvent was removed under reduced pressure

and the resulting catalyst mixture was dried in vacuo (<3 mmHg) at rt for 1 h. To a suspension of 3-crotonoyl-2-oxazolidinone (155 mg, 1.0 mmol) and 4 Å MS (0.5 g) in CH_2Cl_2 (1 mL) was added a solution of the catalyst mixture prepared above in CH_2Cl_2 (4 mL), followed by $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol) and CH_2Cl_2 (1 mL), and finally a solution of the diazoacetophenone (180 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) over a period of 6 h. After removal of the 4 Å MS by filtration (Celite), the reaction mixture was further filtered through a plug of SiO_2 using 50% EtOAc/hexane (100 mL) as eluent. After evaporation of the filtrate under reduced pressure, the residue was purified by column chromatography (20% EtOAc/hexane) to give the cycloadduct as pale yellow prisms (116 mg, 60%): *endo*/*exo* > 99:1 (^{1}H NMR analysis); er 98.0:2.0 (chiral stationary phase HPLC, Daicel Chiralpak IA column); mp 205–206°; $[\alpha]_D^{25}$ −19.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, J = 7.1 Hz, 3H), 2.86 (m, 1H), 3.44–3.51, 3.80–3.89, 4.29–4.43 (m, 4H), 4.46 (d, J = 1.2 Hz, 1H), 4.85 (d, J = 11.9 Hz, 1H), 4.90 (d, J = 5.1 Hz, 1H), 4.95 (d, J = 11.9 Hz, 1H), 7.28–7.36 (m, 2H), 7.46–7.50 (m, 2H), 7.28–7.34, 7.45–7.57, 8.03–8.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 38.6, 43.3, 55.9, 61.9, 65.2, 87.1, 108.9, 121.4, 122.8, 126.7, 129.1, 129.3, 130.1, 131.3, 133.3, 136.5, 142.1, 152.9, 169.9, 193.5.



Dimethyl 1′-Methyl-5-phenyl-2′-oxo-1′,2′-dihydro-5*H*-spiro[furan-2,3′-indole]-3,4-dicarboxylate [Intermolecular Cycloaddition of an Aldehyde-Derived Acyclic Carbonyl Ylide].[88] $Rh_2(OAc)_4$ (3.2 mg, 0.5 mol %) was added to a stirred solution of *N*-methyl-3-diazooxindole (250 mg, 1.45 mmol), benzaldehyde (306 mg, 2.9 mmol), and DMAD (246 mg, 1.73 mmol) in dry CH_2Cl_2 (20 mL) at rt. After 30 min, the reaction mixture was evaporated under reduced pressure and the residue was purified by column chromatography (35% EtOAc/hexane) to give the cycloadduct as a yellow solid (352 mg, 62%): mp 140–142° (hexane/EtOAc); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.19 (s, 3H), 3.57 (s, 3H), 3.68 (s, 3H), 6.49 (s, 1H), 6.82 (d, J = 7.7 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.30–7.48 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.9, 53.0, 89.2, 90.6, 109.2, 123.7, 125.5, 127.2, 128.0, 129.3, 129.8, 131.6, 134.7, 145.1, 145.5, 161.6, 163.1, 174.0.

TABULAR SURVEY

The tables contain all examples that could be found in the literature through the end of 2011. Charts appearing before the Tables show structures of more

complicated catalysts, together with their widely used abbreviations, and assign them numbers for use in the Tables. Cycloadditions in which the carbonyl group forming the ylide is part of the diazo substrate are considered in Tables 1–19, with cycloadditions of acyclic carbonyl ylides in Table 20. For cyclic carbonyl ylides, intramolecular cycloadditions (where usually regio- and stereoselectivity is complete) are presented in Tables 1–8, before intermolecular cycloadditions (Tables 9 onwards). Intra- and intermolecular cycloadditions are further categorized according to the nature of the carbonyl group forming the cyclic carbonyl ylide, with ketones being followed by esters, amides, and imides.

Entries in the tables are ordered by increasing carbon count of the diazo substrate. This count excludes protecting groups, for example the alcohol portion of ester groups, but for a given substrate esters are then ordered in increasing carbon count of the ester group, nitrogen substituents in amides (unless they become part of an ylide-containing ring), *N*-allyl, and *N*- (or *C*-) sulfonyl groups. For a given carbon count, terminal alkenes come before internal, and (*E*) before (*Z*); increasing unsaturation (alkyne comes after alkene). For a given substrate in intermolecular cycloadditions with different dipolarophiles, the carbon count of the dipolarophile orders the dipolarophiles and the same applies for (ester) protecting groups in the dipolarophile. Some entries have been combined in sub-tables with multiple carbon counts. Where relative configuration in the cycloadduct(s) is relevant, the oxygen from the carbonyl ylide is shown 'up', unless absolute configuration is involved and known and dictates otherwise. Unspecified yields are indicated by (—).

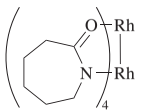
The following abbreviations (excluding those listed in "The *Journal of Organic Chemistry* Standard Abbreviations and Acronyms) were used in the text and the Tabular Survey:

p-ABSA	*p*-acetamidobenzenesulfonyl azide
acm	acetamidomethyl
adc	adamantanylcarboxylate
ATPH	aluminum tris(2,6-diphenylphenoxide)
bbim	1,3-dibutylimidazolium
BIEP	bis(isoequilenine) phosphate
BINIM	binaphthyldiimine
BINOL	2,2′-dihydroxy-1,1′-binaphthyl
bmim	1-butyl-3-methylimidazolium
BNP	binaphthol phosphate
(*S*)-BPTA	*N*-benzene-fused-phthaloyl-(*S*)-alaninate
(*S*)-BPTPA	*N*-benzene-fused-phthaloyl-(*S*)-phenylalaninate
(*S*)-BPTTL	*N*-benzene-fused-phthaloyl-(*S*)-*tert*-leucinate
(*S*)-BPTV	*N*-benzene-fused-phthaloyl-(*S*)-valinate
cap	caprolactamate
DBBNP	3,3′-dibromobinaphthol phosphate
DDBNP	6,6′-didodecylbinaphthol phosphate
de	diastereoisomeric excess

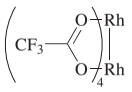
DMAD	dimethyl acetylenedicarboxylate
DMBNP	3,3′-dimethylbinaphthol phosphate
DOSP	*N*-(*p*-dodecylphenyl)sulfonylprolinate
dppp	1,3-bis(diphenylphosphino)propane
eq	equivalents
esp	3,3′-(1,3-phenylene)bis(2,2-dimethylpropanoate)
exp	experimental
Fc	ferrocenyl
hfacac	hexafluoroacetylacetonate
L.A.	Lewis acid
MAD	methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide)
man	mandelate
MEK	methyl ethyl ketone
MEOX	methyl 2-oxazolidinone-4-carboxylate
MEPY	methyl 2-oxopyrrolidine-5-carboxylate
mmim	1,3-dimethylimidazolium
MPA	α-methoxyphenylacetate
MS	molecular sieves
n. d.	not determined
(*S*)-NTPA	*N*-naphth-1,8-dioyl-(*S*)-alaninate
(*S*)-NTTL	*N*-naphth-1,8-dioyl-(*S*)-*tert*-leucinate
(*S*)-NTPV	*N*-naphth-1,8-dioyl-(*S*)-valinate
NPM	*N*-phenylmaleimide
oct	octanoate
PEG	poly(ethylene glycol)
pfb	perfluorobutyrate
pfbm	perfluorobutyramidate
PMP	4-methoxyphenyl
(*S*)-PTA	*N*-phthaloyl-(*S*)-alaninate
(*S*)-PTPA	*N*-phthaloyl-(*S*)-phenylalaninate
(*S*)-PTTL	*N*-phthaloyl-(*S*)-*tert*-leucinate
(*S*)-PTV	*N*-phthaloyl-(*S*)-valinate
pwd.	powdered
Pybox	pyridine bisoxazoline
QN	quinolinyl
TBDPS	*tert*-butyldiphenylsilyl
TBQ	tetrachloro-l,2-benzoquinone
TBSP	*N*-(4-*tert*-butylphenyl)sulfonylprolinate
(*S*)-TCPTTL	*N*-tetrachlorophthaloyl-(*S*)-*tert*-leucinate
(*S*)-TFPTTL	*N*-tetrafluorophthaloyl-(*S*)-*tert*-leucinate
TDCPP	*meso*-tetrakis(2,6-dichlorophenyl)porphyrin
TES	triethylsilyl
tfa	trifluoroacetate
tfb	2,4,6-trifluorobenzoate
TIPB	1,3,5-triisopropylbenzene

TMeP	*meso*-tetrakis(mesityl)porphyrin
TMP	1,2,6-trimethylpiperidine
Tol	*p*-tolyl, 4-methylphenyl
tpa	triphenylacetate
4-F-TPP	*meso*-tetrakis(4-fluorophenyl)porphyrin
4-MeO-TPP	*meso*-tetrakis(4-methoxyphenyl)porphyrin
TPS	triphenylsilyl
TTP	*meso*-tetrakis(4-tolyl)porphyrin

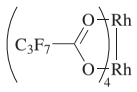
CHART 1. NON-CHIRAL CATALYST COMPLEXES



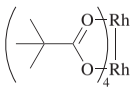
$Rh_2(cap)_4$



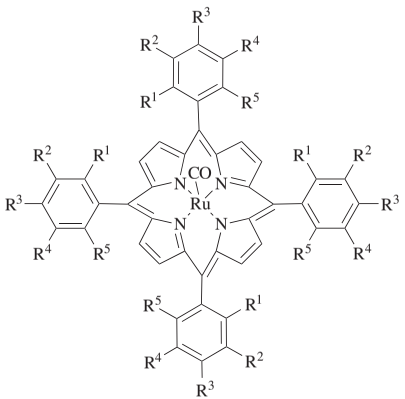
$Rh_2(tfa)_4$



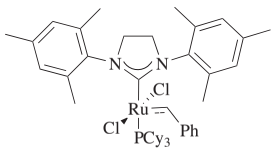
$Rh_2(pfb)_4$



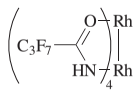
$Rh_2(Opiv)_4$



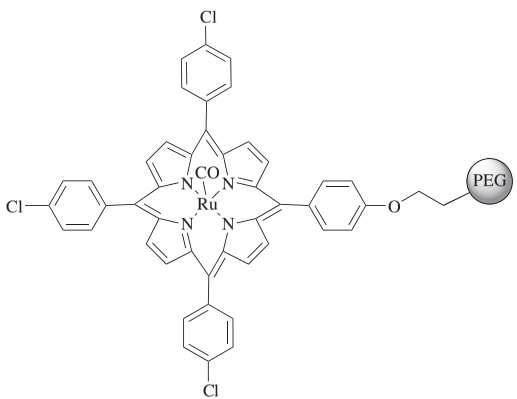
	R^1	R^2	R^3	R^4	R^5	
1a:	H	H	Me	H	H	Ru(TTP)(CO)
1b:	H	H	F	H	H	Ru(4-F-TPP)(CO)
1c:	H	H	MeO	H	H	Ru(4-MeO-TPP)(CO)
1d:	Me	H	Me	H	Me	Ru(TMeP)(CO)
1e:	Cl	H	H	H	Cl	Ru(TDCPP)(CO)
1f:	F	F	F	F	F	Ru(F_{20}-TPP)(CO)



Grubbs' second generation catalyst

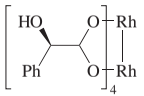


$Rh_2(pfbm)_4$



2: Ru-PEG

CHART 2. CHIRAL CATALYST COMPLEXES AND LIGANDS



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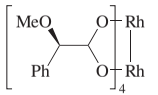
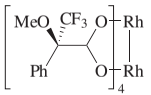


4: $Rh_2[(R)\text{-MPA}]_4$



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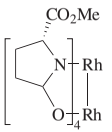
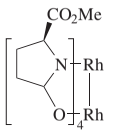
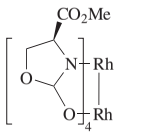


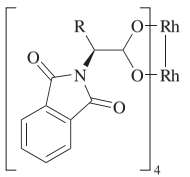
(*R*)-**6**: $Rh_2[(R)\text{-MEPY}]_4$



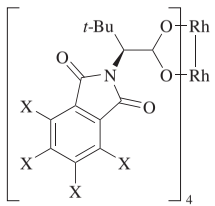
(*S*)-**6**: $Rh_2[(S)\text{-MEPY}]_4$



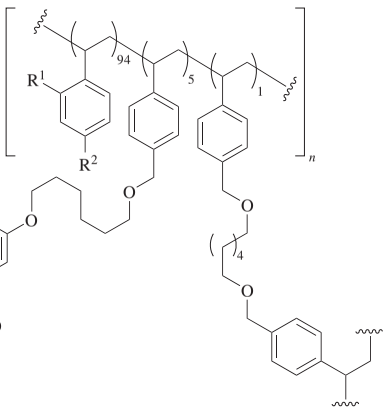
7: $Rh_2[(S)\text{-MEOX}]_4$

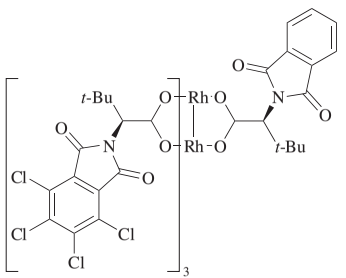


	R	
8a:	Bn	$Rh_2[(S)\text{-PTPA}]_4$
8b:	Me	$Rh_2[(S)\text{-PTA}]_4$
8c:	*i*-Pr	$Rh_2[(S)\text{-PTV}]_4$
8d:	*t*-Bu	$Rh_2[S)\text{-PTTL}]_4$

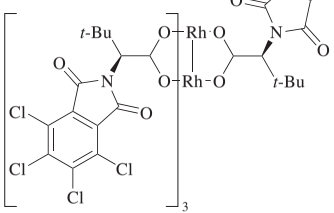


	X	
8e:	F	$Rh_2[(S)\text{-TFPTTL}]_4$
8f:	Cl	$Rh_2[(S)\text{-TCPTTL}]_4$

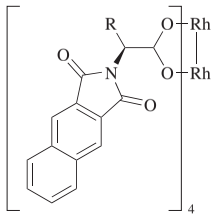




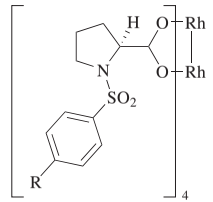
8g: $Rh_2[(S)\text{-PTTL}][(S)\text{-TCPTTL}]_3$



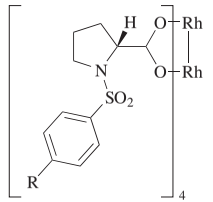
	R^1	R^2
8h:	H	H
8i:	H	CF_3
8j:	CF_3	H



R		
9a:	Bn	Rh_2[(*S*)-BPTPA]$_4$
9b:	Me	Rh_2[(*S*)-BPTA]$_4$
9c:	*i*-Pr	Rh_2[(*S*)-BPTV]$_4$
9d:	*t*-Bu	Rh_2[(*S*)-BPTTL]$_4$

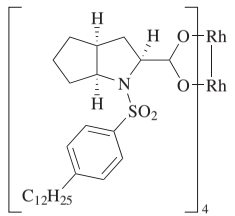


R		
10a:	*t*-Bu	Rh_2[(*S*)-TBSP]$_4$
10b:	*n*-$C_{12}H_{25}$	Rh_2[(*S*)-DOSP]$_4$



(*R*)-**10b**: Rh_2[(*R*)-DOSP]$_4$

R = *n*-$C_{12}H_{25}$



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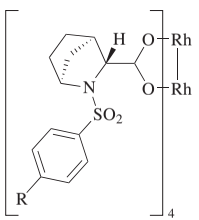
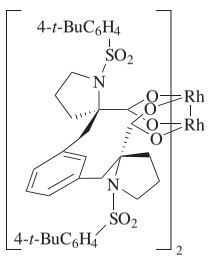


R	
12a:	*t*-Bu
12b:	*n*-$C_{12}H_{25}$



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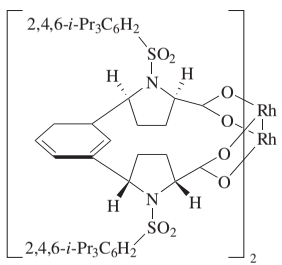

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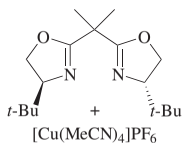
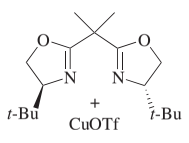
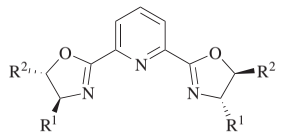


15•[Cu(MeCN)$_4$]PF$_6$

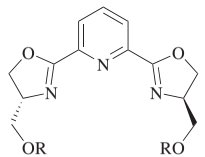


15•CuOTf

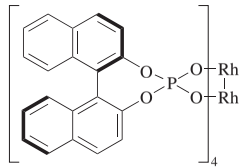
CHART 2. CHIRAL CATALYST COMPLEXES AND LIGANDS (*Continued*)



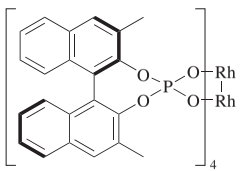
	R^1	R^2	
16a:	*i*-Pr	H	(*S*,*S*)-Pybox-*i*-Pr
16b:	Ph	H	(*S*,*S*)-Pybox-Ph
16c:	Ph	Ph	(4*S*,5*S*)-Pybox-4,5-Ph_2



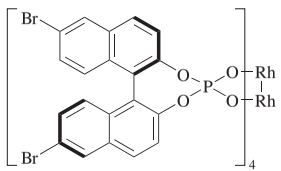
	R	
17a:	H	(*S*,*S*)-Pybox-Hm
17b:	TBS	(*S*,*S*)-Pybox-TBSm
17c:	*t*-BuPh_2Si	(*S*,*S*)-Pybox-TBDPSm
17d:	Ph_3Si	(*S*,*S*)-Pybox-TPSm



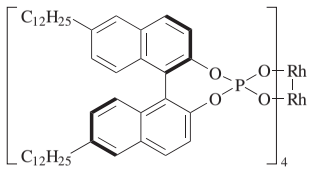
18: Rh_2[(*R*)-BNP]$_4$



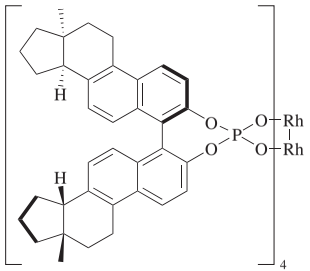
19: Rh_2[(*R*)-DMBNP]$_4$



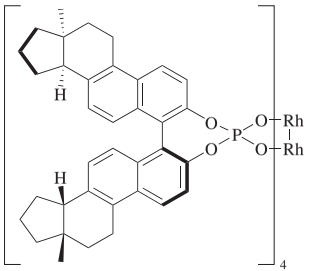
20: Rh_2[(*R*)-DBBNP]$_4$



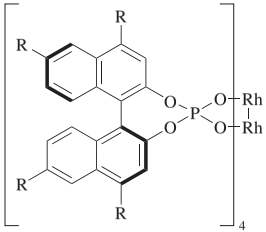
21: Rh_2[(*R*)-DDBNP]$_4$



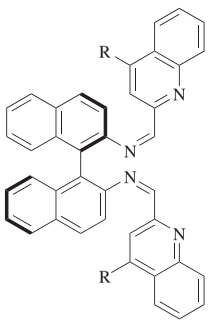
(*R*,*S*)-**22**: Rh_2[(*R*,*S*)-BIEP]$_4$



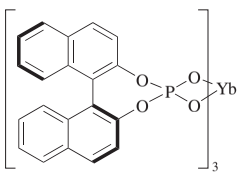
(*S*,*S*)-**22**: Rh_2[(*S*,*S*)-BIEP]$_4$



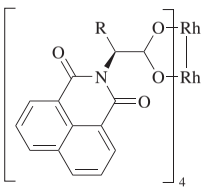
	R
23a:	Ph
23b:	4-*n*-BuC_6H_4
23c:	$PhCH_2CH_2$
23d:	*n*-C_8H_{17}



	R	
24a:	H	(*R*)-BINIM-2QN
24b:	Me	(*R*)-BINIM-4-Me-2QN
24c:	3,5-$Me_2C_6H_3$	(*R*)-BINIM-4-(3,5-xylyl)-2QN

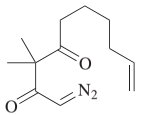
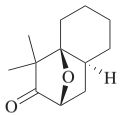
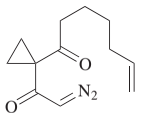
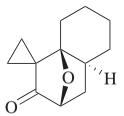
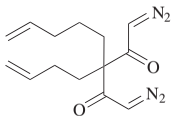
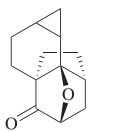
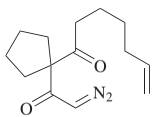
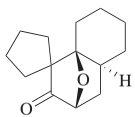
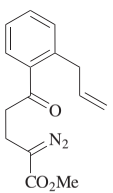
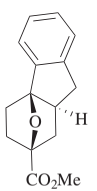


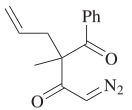
25: Yb[(*S*)-BNP]$_3$



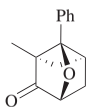
	R	
26a:	Bn	Rh_2[(*S*)-NTPA]$_4$
26b:	*t*-Bu	Rh_2[(*S*)-NTTL]$_4$
26c:	*i*-Pr	Rh_2[(*S*)-NTV]$_4$

TABLE 1. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (50)	58
	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (98)	58
C_{13} 	$(EtO)_3P{\bullet}CuCl$, C_6H_6	 (36)	60
C_{14} 	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (75)	58
	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (80)	120

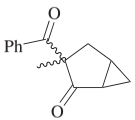


Catalyst, CH_2Cl_2, rt



I

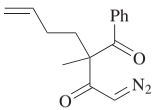
+



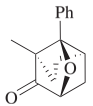
II

Catalyst	**I**	**II**	
$Rh_2(OAc)_4$	(60)	(24)	54, 64
$Rh_2(tfa)_4$	(67)	(0)	
$Rh_2(cap)_4$	(70)	(28)	

C_{15}

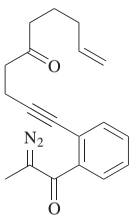


$Rh_2(OAc)_4$, CH_2Cl_2, rt

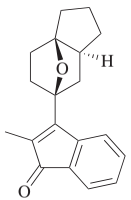


(>95) 54

C_{19}



Catalyst, CH_2Cl_2, rt



(97)

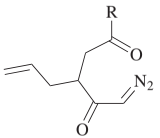
Catalyst	
$Rh_2(oct)_4$	108
$Rh_2(OAc)_4$	107

TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES

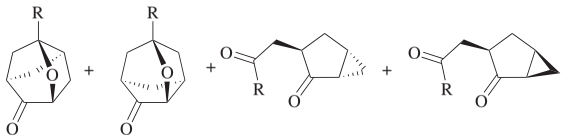
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*

C_{9-14}



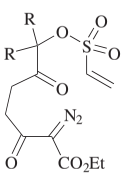
Catalyst, rt



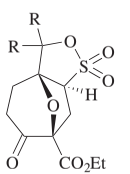
I **II** **III** **IV**

R	Catalyst	Solvent	I + II + III + IV	I/II/III/IV	I/III	
Me	$Rh_2(OAc)_4$	C_6H_6	(—)	—	1:1	65
Me	$Rh_2(OAc)_4$	CH_2Cl_2	(83)	6:41:22:14	—	54
Me	$Rh_2(cap)_4$	CH_2Cl_2	(82)	8:25:34:15	—	54
Me	$Rh_2(pfb)_4$	CH_2Cl_2	(58)	0:18:27:13	—	54
Me	$Rh_2(tfa)_4$	CH_2Cl_2	(71)	0:35:24:12	—	54
Me	$Cu(acac)_2$	CH_2Cl_2	(94)	0:9:75:10	—	54
Me	$PdCl_2(PhCN)_2$	CH_2Cl_2	(89)	0:0:83:6	—	54
Ph	$Rh_2(OAc)_4$	CH_2Cl_2	(94)	10:47:23:14	—	54, 64
Ph	$Rh_2(cap)_4$	CH_2Cl_2	(96)	12:52:28:4	—	54, 64
Ph	$Rh_2(pfb)_4$	CH_2Cl_2	(87)	33:12:25:17	—	54
Ph	$Rh_2(tfa)_4$	CH_2Cl_2	(93)	34:12:17:30	—	54, 64
Ph	$Cu(acac)_2$	CH_2Cl_2	(98)	9:35:34:20	—	54
Ph	$PdCl_2(PhCN)_2$	CH_2Cl_2	(68)	0:0:38:30	—	54

C_{9-11}



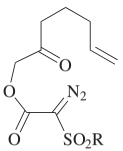
$Rh_2(oct)_4$, CH_2Cl_2, 0°



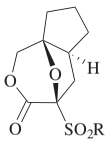
R	
H	(75)
Me	(86)

68

C_9



Catalyst, rt



R	Catalyst	Solvent		er
Me	$Rh_2(OAc)_4$	toluene	(20)	—
Me	$Rh_2(oct)_4$	toluene	(43)	—
Me	**9c**	$PhCF_3$	(80)	66.5:33.5
Ph	$Rh_2(OAc)_4$	toluene	(12)	—
Ph	$Rh_2(tfa)_4$	toluene	(39)	—
Ph	$Rh_2(cap)_4$	toluene	(0)	—
Ph	$Rh_2(oct)_4$	toluene	(72)	—
Ph	**10b**	toluene	(67)	52.0:48.0
Ph	**21**	toluene	(67)	54.5:45.5
Ph	**8a**	$PhCF_3$	(37)	63.5:36.5
Ph	**8d**	$PhCF_3$	(80)	67.0:33.0
Ph	**9c**	$PhCF_3$	(75)	71.5:28.5

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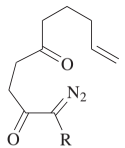
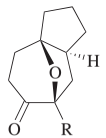
TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

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

C_{10-16}

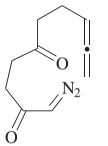


Catalyst

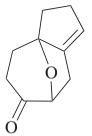


R	Catalyst	Solvent	Temp		er	Refs.
H	$Rh_2(OAc)_4$	C_6H_6	rt	(75)	—	43, 109, 290
H	**1a**	CH_2Cl_2	rt	(83)	—	171
Ph	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(77)	—	46
Ph	**10b**	CH_2Cl_2	rt	(71)	52.5:47.5	46
Ph	**10b**	hexane	rt	(75)	56.0:44.0	46
Ph	**18**	hexane	rt	(41)	65.0:35.0	46
Ph	**18**	hexane	reflux	(81)	59.5:40.5	46
Ph	**18**	$PhCF_3$	rt	(67)	53.0:47.0	46
Ph	**21**	CH_2Cl_2	rt	(51)	55.0:45.0	46
Ph	**21**	hexane	rt	(87)	67.5:32.5	46
Ph	**21**	hexane	reflux	(87)	59.5:40.5	46
Ph	**9c**	CH_2Cl_2	rt	(50)	53.5:46.5	46
Ph	**9c**	hexane	rt	(49)	55.5:44.5	46
Ph	**9c**	$PhCF_3$	rt	(74)	57.0:43.0	46
4-$O_2NC_6H_4$	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(>99)	—	46
4-$O_2NC_6H_4$	**10b**	hexane	rt	(>99)	54.0:46.0	46
4-$O_2NC_6H_4$	**18**	hexane	reflux	(97)	60.0:40.0	46
4-$O_2NC_6H_4$	**21**	CH_2Cl_2	rt	(63)	54.0:46.0	46
4-$O_2NC_6H_4$	**21**	hexane	rt	(>99)	75.6:24.5	46
4-$O_2NC_6H_4$	**21**	hexane	reflux	(>99)	64.0:36.0	46
4-$O_2NC_6H_4$	**9c**	$PhCF_3$	rt	(98)	56.5:43.5	46

C_{10}

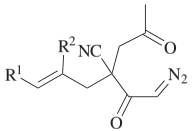


$Rh_2(OAc)_4$, CH_2Cl_2, 0°

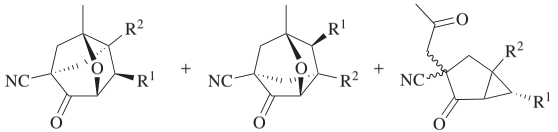


(73)

124

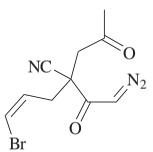


Catalyst CH_2Cl_2, rt

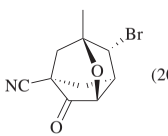


I **II** **III**

R^1	R^2	Catalyst	**I**	**II**	**III**	
H	H	$Rh_2(OAc)_4$	(trace)	(65)	(8)	55
H	H	$Rh_2(tfa)_4$	(trace)	(80)	(trace)	55
H	Br	$Rh_2(OAc)_4$	(0)	(68)	(0)	55
Cl	H	$Rh_2(OAc)_4$	(90)	(—)	(—)	69
Br	H	$Rh_2(OAc)_4$	(82)	(9)	(7)	55, 69
I	H	$Rh_2(OAc)_4$	(83)	(8)	(8)	55, 69

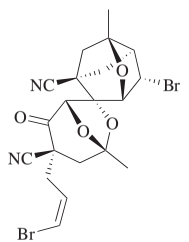


$Rh_2(OAc)_4$, CH_2Cl_2, rt



(20)

+



(20)

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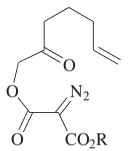
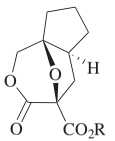
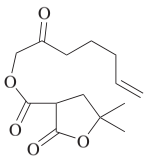
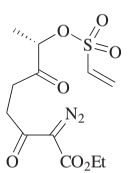
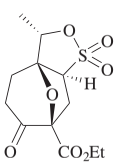
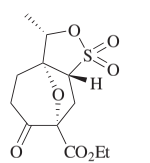
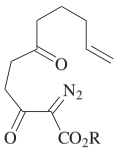
TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	Catalyst	 +  **I** **II**	

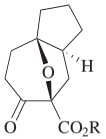
R	Catalyst	Solvent	Temp	**I**	er	**II**	
Et	$Rh_2(OAc)_4$	C_6H_6	90°	(67)	—	(—)	43, 162, 291
t-Bu	$Rh_2(OAc)_4$	CH_2Cl_2	reflux	(46)	—	(—)	57
t-Bu	$Rh_2(OAc)_4$	C_6H_6	reflux	(74)	—	(—)	57
t-Bu	**10b**	CH_2Cl_2	reflux	(54)	50.5:49.5	(21)	57
t-Bu	**10b**	hexane	reflux	(41)	52.5:47.5	(6)	57
t-Bu	**10b**	C_6H_6	reflux	(57)	51.5:48.5	(—)	57
t-Bu	**9c**	$PhCF_3$	rt	(39)	50.0:50.0	(20)	57
t-Bu	**18**	CH_2Cl_2	rt	(27)	57.0:43.0	(39)	57
t-Bu	**18**	CH_2Cl_2	reflux	(24)	56.5:43.5	(25)	57
t-Bu	**18**	hexane	reflux	(27)	59.0:41.0	(—)	57
t-Bu	**18**	C_6H_6	reflux	(47)	55.5:44.5	(9)	57
t-Bu	**21**	hexane	rt	(12)	71.5:28.5	(—)	57

	$Rh_2(oct)_4$, CH_2Cl_2, 0°	 +  **I** **II**	**I** + **II** (61) **I/II** = 7:1	68

C_{11}

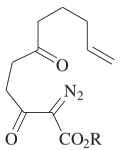
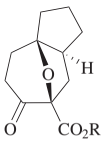


Catalyst



R	Catalyst	Solvent	Temp		er	
Me	**10b**	hexane	0°	(65)	66.5:33.5	95
Me	**10b**	hexane	rt	(86)	74.0:26.0	292
Me	**10b**	hexane	reflux	(96)	74.0:26.0	95
Me	**18**	C_6H_6	rt	(70)	54.0:46.0	95
Me	**19**	CH_2Cl_2	rt	(76)	52.0:48.0	95
Me	**19**	C_6H_6	rt	(73)	63.0:37.0	95
Me	**21**	CH_2Cl_2	rt	(77)	53.5:46.5	95
Me	**21**	hexane	rt	(72)	60.0:40.0	95
Me	**21**	C_6H_6	rt	(57)	55.0:45.0	95
Et	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(73)	—	292
Et	(*R*)-**6**	CH_2Cl_2	rt	(75)	50.0:50.0	292
Et	**10b**	CH_2Cl_2	rt	(—)	54.0:46.0	292
Et	**10b**	hexane	0°	(63)	76.0:24.0	95, 292
Et	**10b**	hexane	rt	(82)	76.0:24.0	95, 292
Et	**10b**	hexane	reflux	(90)	64.5:35.5	95, 292
t-Bu	**15**•$[Cu(MeCN)_4]PF_6$	CH_2Cl_2	reflux	(25)	50.0:50.0	292
t-Bu	**3**	CH_2Cl_2	rt	(93)	55.5:44.5	292
t-Bu	**3**	hexane	rt	(48)	54.5:45.5	292
t-Bu	**4**	CH_2Cl_2	rt	(97)	58.0:42.0	292
t-Bu	**4**	hexane	rt	(92)	61.0;39.0	292
t-Bu	**5**	CH_2Cl_2	rt	(98)	58.5:41.5	292
t-Bu	**5**	hexane	rt	(95)	54.5:45.5	292
t-Bu	**8a**	CH_2Cl_2	rt	(87)	64.0:36.0	292
t-Bu	**8a**	hexane	rt	(55)	60.5:39.5	292
t-Bu	**8d**	CH_2Cl_2	rt	(72)	61.5:38.5	292

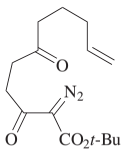
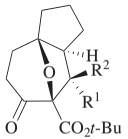
TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)						Refs.
C_{11}		R	Catalyst	Solvent	Temp		er	
	Catalyst	*t*-Bu	**8d**	hexane	reflux	(86)	60.0:40.0	95
		*t*-Bu	**8d**	Et_2O	rt	(60)	57.0:43.0	95, 292
		t-Bu	**10a**	hexane	rt	(59)	69.0:31.0	95
		t-Bu	**10b**	CH_2Cl_2	rt	(86)	55.0:45.0	95
		t-Bu	**10b**	hexane	rt	(93)	76.0:24.0	95
		t-Bu	**10b**	hexane	43°	(84)	74.0:26.0	95
		t-Bu	**10b**	hexane	reflux	(89)	71.0:29.0	95
		t-Bu	**10b**	hexane	0°	(74)	75.5:24.5	95
		t-Bu	**10b**	hexane	−7°	(55)	74.0:26.0	95
		t-Bu	**11**	CH_2Cl_2	rt	(81)	56.5:43.5	95
		t-Bu	**11**	hexane	rt	(75)	65.5:34.5	95
		t-Bu	**12a**	CH_2Cl_2	rt	(43)	58.5:41.5	95
		t-Bu	**12a**	hexane	rt	(60)	67.0:33.0	95
		t-Bu	**12b**	CH_2Cl_2	rt	(87)	58.0:42.0	95
		t-Bu	**12b**	hexane	rt	(65)	66.0:34.0	95
		t-Bu	**13**	CH_2Cl_2	rt	(71)	60.0:40.0	95
		t-Bu	**13**	hexane	rt	(51)	68.0:32.0	95
		t-Bu	**14**	$CHCl_2$	rt	(55)	61.0:39.0	95
		t-Bu	**14**	hexane	rt	(65)	61.0:39.0	95
		t-Bu	**9c**	$PhCF_3$	rt	(90)	50.5:49.5	95, 115
		t-Bu	**18**	CH_2Cl_2	rt	(83)	82.5:17.5	95, 115
		t-Bu	**18**	CH_2Cl_2	0°	(55)	82.0:18.0	95, 115
		t-Bu	**18**	hexane	rt	(65)	82.0:18.0	95, 115
		t-Bu	**18**	C_6H_6	rt	(55)	66.5:33.5	95
		t-Bu	**19**	CH_2Cl_2	rt	(50)	53.5:46.5	95, 115
		t-Bu	**19**	C_6H_6	rt	(30)	63.0:37.0	95
		t-Bu	**20**	CH_2Cl_2	rt	(67)	79.0:21.0	95, 115
		t-Bu	**20**	CH_2Cl_2	0°	(36)	80.5:19.5	95, 115

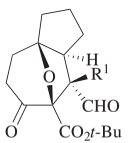
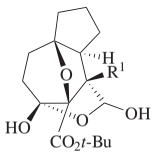
(Continued)

t-Bu	**20**	hexane	rt	(34)	83.0:17.0	95, 115
t-Bu	**21**	CH_2Cl_2	rt	(80)	84.0:16.0	95, 115
t-Bu	**21**	hexane	rt	(76)	90.5:9.5	95, 115
t-Bu	**21**	hexane	0°	(81)	94.5:5.5	95, 115
t-Bu	**21**	hexane	−15°	(86)	95.0:5.0	95, 115
t-Bu	(*R*,*S*)-**22**	CH_2Cl_2	rt	(47)	77.5:22.5	95
t-Bu	(*R*,*S*)-**22**	hexane	rt	(65)	87.5:12.5	95
t-Bu	(*R*,*S*)-**22**	hexane	0°	(35)	87.0:13.0	95
t-Bu	(*S*,*S*)-**22**	CH_2Cl_2	rt	(60)	79.5:20.5	95
t-Bu	(*S*,*S*)-**22**	hexane	rt	(66)	88.5:11.5	95
t-Bu	(*S*,*S*)-**22**	hexane	0°	(42)	90.0:10.0	95
t-Bu	**23a**	CH_2Cl_2	20°	(20)	52.5:47.5	116
t-Bu	**23a**	hexane	20°	(trace)	—	116
t-Bu	**23a**	$PhCF_3$	20°	(35)	55.5:44.5	116
t-Bu	**23b**	CH_2Cl_2	20°	(35)	25.0:75.0	116
t-Bu	**23b**	hexane	20°	(48)	18.5:81.5	116
t-Bu	**23c**	CH_2Cl_2	20°	(48)	23.0:77.0	116
t-Bu	**23c**	$CHCl_2$	0°	(47)	17.0:83.0	116
t-Bu	**23c**	hexane	20°	(24)	31.5:68.5	116
t-Bu	**23d**	CH_2Cl_2	20°	(86)	15.0:85.0	116
t-Bu	**23d**	CH_2Cl_2	0°	(75)	12.0:88.0	116
t-Bu	**23d**	CH_2Cl_2	−15°	(64)	10.5:89.5	116
t-Bu	**23d**	CH_2Cl_2	−30°	(32)	11.0:89.0	116
t-Bu	**23d**	hexane	20°	(76)	9.0:91.0	116
t-Bu	**23d**	hexane	0°	(72)	10.0:90.0	116
t-Bu	**23d**	hexane	−15°	(75)	7.0:93.0	116
t-Bu	**23d**	hexane	−30°	(49)	7.5:92.5	116

TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

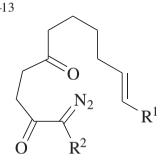
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	1.  Grubbs' 2nd-gen Ru cat. (5 mol %), CH_2Cl_2, reflux 2. $Rh_2(OAc)_4$, CH_2Cl_2, rt		121, 122

R^1	R^2	R^3	
Me	Me	Me	(79)
MeO_2C	H	H	(69)
Cy	H	H	(63)
Ph	H	H	(73)
4-FC_6H_4	H	H	(75)
2-ClC_6H_4	H	H	(80)
4-ClC_6H_4	H	H	(68)
4-$O_2NC_6H_4$	H	H	(76)
4-$MeOC_6H_4$	H	H	(43)
4-MeC_6H_4	H	H	(77)

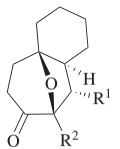
	1.  Grubbs' 2nd-gen Ru cat. (5 mol %), CH_2Cl_2, reflux 2. $Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** +  **II**		

R^1	R^2	**I + II**	**I/II**	
H	Me	(70)	4:1	122
Me	H	(86)	1:1	121, 122

C_{11-13}

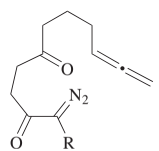


Catalyst

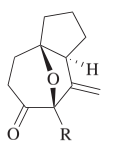


R^1	R^2	Catalyst	Solvent	Temp		er	
H	H	$Rh_2(OAc)_4$	C_6H_6	rt	(60)	—	43
H	t-BuO_2C	**10b**	hexane	rt	(77)	74.0:26.0	37, 45, 43
H	t-BuO_2C	**21**	CH_2Cl_2	rt	(50)	78.5:21.5	57, 126, 292, 127
H	t-BuO_2C	**21**	hexane	rt	(73)	92.5:7.5	57, 126
H	t-BuO_2C	**21**	hexane	0°	(68)	93.5:6.5	57, 126
Me	t-BuO_2C	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(30)	—	127
Me	t-BuO_2C	**10b**	CH_2Cl_2	rt	(43)	61.0:39.0	127
Me	t-BuO_2C	**10b**	hexane	rt	(31)	74.5:25.5	57, 126
Me	t-BuO_2C	**21**	CH_2Cl_2	rt	(31)	74.0:26.0	127
Me	t-BuO_2C	**21**	hexane	rt	(44)	75.5:24.5	57, 126
Me	t-BuO_2C	**21**	hexane	0°	(44)	79.5:20.5	57, 126
MeO_2C	t-BuO_2C	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(78)	—	127
MeO_2C	t-BuO_2C	**10b**	CH_2Cl_2	rt	(66)	50.0:50.0	127
MeO_2C	t-BuO_2C	**10b**	hexane	rt	(63)	55.0:45.0	57
MeO_2C	t-BuO_2C	**9c**	$PhCF_3$	rt	(95)	58.5:41.5	57
MeO_2C	t-BuO_2C	**21**	hexane	rt	(70)	60.5:39.5	57
MeO_2C	t-BuO_2C	**21**	hexane	0°	(57)	66.0:34.0	57

C_{11-12}



$Rh_2(OAc)_4$, CH_2Cl_2

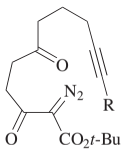


R	Temp		
H	0°	(74)	124
EtO_2C	rt	(50)	

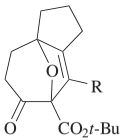
TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

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

C_{11-12}

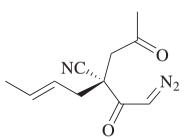


Catalyst

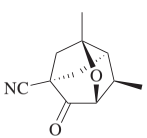


R	Catalyst	Solvent	Temp		er	
H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(70)	—	127
H	**10b**	CH_2Cl_2	rt	(85)	56.0:44.0	127
H	**10b**	hexane	rt	(83)	78.5:21.5	57, 126
H	**21**	CH_2Cl_2	rt	(60)	84.5:15.5	127
H	**21**	hexane	rt	(77)	87.0:13.0	57, 126
H	**21**	hexane	0°	(80)	93.0:7.0	57, 126
H	**21**	hexane	−15°	(42)	92.5:7.5	57, 126
Me	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(78)	—	127
Me	**10b**	CH_2Cl_2	rt	(81)	64.5:35.5	127
Me	**10b**	hexane	rt	(74)[a]	69.5:30.5	126
Me	**10b**	hexane	rt	(77)[b]	75.0:25.0	57
Me	**21**	CH_2Cl_2	rt	(75)	73.0:27.0	127
Me	**21**	hexane	rt	(76)	80.0:20.0	57, 126
Me	**21**	hexane	0°	(68)	84.0:16.0	57, 126
Me	**21**	hexane	−15°	(66)	88.0:12.0	57, 126

C_{11}

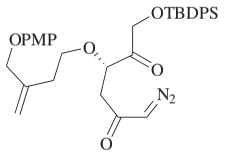


$Rh_2(OAc)_4$, CH_2Cl_2, rt

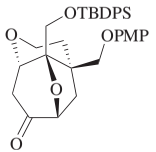


(55) 69

C_{11}

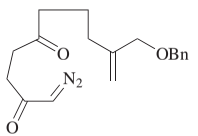


Catalyst

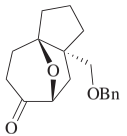


Catalyst	Solvent	Temp (°)		
$Rh_2(OCOC_7H_{15})_4$	—	—	(trace)	
$Rh_2(OCOCPh_3)_4$	—	—	(24)	
$Rh_2(NHAc)_4$	—	—	(41)	67
$Rh_2(OAc)_4$	C_6H_6	—	(57)	
$Rh_2(OAc)_4$	CH_2Cl_2	—	(31)	
$Rh_2(OAc)_4$	toluene	60	(36)	
$Rh_2(OAc)_4$	toluene	110	(68)	
$Rh_2(OAc)_4$	$PhCF_3$	100	(73)	

C_{12}



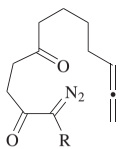
$Rh_2(OAc)_4$, C_6H_6, rt



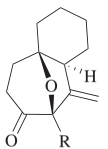
(61)

70, 71

C_{12-13}

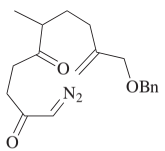


$Rh_2(OAc)_4$, CH_2Cl_2, rt

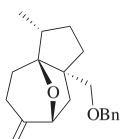


R	
H	(71)
EtO_2C	(79)

124

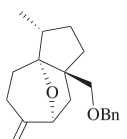


$Rh_2(OAc)_4$, CH_2Cl_2, 0°



I

+

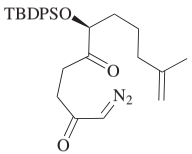
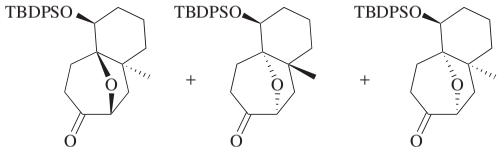


II

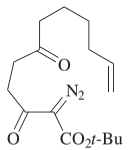
I + **II** (63)
I/**II** = 4:1

70, 71

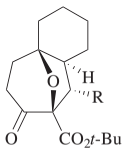
TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	Catalyst, 4 Å MS	 **I** + **II** + **III** (<5)	76

Catalyst	Solvent	Temp (°)	**I** + **II**	**I/II**
$Rh_2(oct)_4$	CH_2Cl_2	rt	(77)	2.7:1
$Rh_2(oct)_4$	CH_2Cl_2	0	(81)	3.1:1
$Rh_2(oct)_4$	CH_2Cl_2	−15	(74)	3.1:1
$Rh_2(oct)_4$	hexane	0	(60)	3.6:1
$Rh_2(oct)_4$	$PhCF_3$	0	(50)	3.5:1
$Rh_2(OAc)_4$	CH_2Cl_2	rt	(64)	3.3:1
$Rh_2(OAc)_4$	CH_2Cl_2	0	(65)	3.1:1
$Rh_2(OAc)_4$	CH_2Cl_2	−15	(65)	2.3:1
$Rh_2(OAc)_4$	hexane	0	(<15)	—
$Rh_2(OAc)_4$	$PhCF_3$	0	(<15)	—
$Rh_2(tfa)_4$	CH_2Cl_2	0	(<15)	—
(*R*)-**10b**	CH_2Cl_2	0	(82)	2.3:1
10b	CH_2Cl_2	0	(58)	2.9:1
26a	CH_2Cl_2	0	(78)	3.1:1
26b	CH_2Cl_2	0	(68)	3.5:1
26c	CH_2Cl_2	0	(68)	3.3:1
9c	CH_2Cl_2	0	(52)	2.7:1

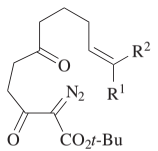


1. ,
Grubbs' 2nd-gen Ru cat.
(5 mol %), CH_2Cl_2, reflux
2. $Rh_2(OAc)_4$, CH_2Cl_2, rt

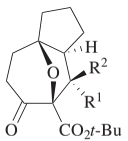


R		
MeO_2C	(63)	122
Cy	(50)	
Ph	(66)	

$C_{12–17}$



Catalyst

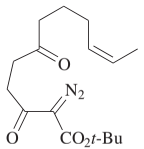


R^1	R^2	Catalyst	Solvent	Temp		er	
Me	H	**10b**	CH_2Cl_2	rt	(36)	64.0:36.0	127
Me	H	**10b**	hexane	rt	(66)	76.5:23.5	57, 126
Me	H	**21**	CH_2Cl_2	rt	(53)	76.0:24.0	127
Me	H	**21**	hexane	rt	(63)	82.0:18.0	57, 126
Me	H	**21**	hexane	0°	(65)	86.0:14.0	57, 126
Me	H	**21**	hexane	−15°	(53)	90.0:10.0	57, 126
Me	Me	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(74)	—	121, 122
MeO_2C	H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(89)	—	121, 122
MeO_2C	H	**10b**	CH_2Cl_2	rt	(88)	54.0:46.0	127
MeO_2C	H	**10b**	hexane	rt	(74)	65.5:34.5	57
MeO_2C	H	**9c**	$PhCF_3$	rt	(93)	59.0:41.0	57
MeO_2C	H	**21**	hexane	rt	(86)	67.5:32.5	57
MeO_2C	H	**21**	hexane	0°	(83)	69.0:31.0	57
Cy	H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(78)	—	121, 122

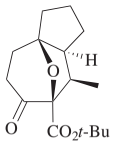
TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

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

C_{12}

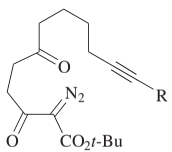


Catalyst

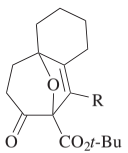


Catalyst	Solvent	Temp		er	
$Rh_2(OAc)_4$	CH_2Cl_2	rt	(75)	—	127
10b	CH_2Cl_2	rt	(67)	63.5:36.5	127
10b	hexane	rt	(68)	71.0:29.0	57, 126
21	CH_2Cl_2	rt	(71)	—	127
21	hexane	rt	(67)	87.5:12.5	57, 126
21	hexane	0°	(57)	90.0:10.0	57, 126
21	hexane	−15°	(49)	91.5:8.5	57, 126

C_{12-13}

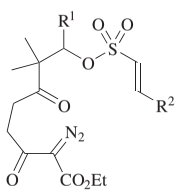


Catalyst

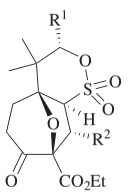


R	Catalyst	Solvent	Temp		er	
H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(59)	—	127
H	**10b**	hexane	rt	(33)	62.0:38.0	57, 126
H	**21**	CH_2Cl_2	rt	(45)	59.0:41.0	127
H	**21**	hexane	rt	(41)	86.5:13.5	57, 126
H	**21**	hexane	0°	(41)	93.0:7.0	57, 126
Me	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(29)	—	127
Me	**10b**	CH_2Cl_2	rt	(47)	55.0:45.0	127
Me	**10b**	hexane	rt	(73)	84.5:15.5	57, 126
Me	**21**	CH_2Cl_2	rt	(40)	68.0:32.0	127
Me	**21**	hexane	rt	(38)	83.5:16.5	57, 126
Me	**21**	hexane	0°	(47)	89.5:10.5	57, 126
Me	**21**	hexane	−15°	(19)	87.0:13.0	127

C_{12-18}

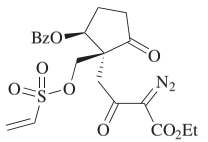


$Rh_2(oct)_4$, CH_2Cl_2

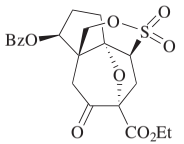


R^1	R^2	Temp		dr	
H	H	0°	(92)	—	
Me	H	rt	(93)	>20:1	68
H	Ph	0°	(88)	—	
H	4-FC_6H_4	0°	(88)	—	

C_{12}



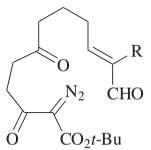
$Rh_2(OAc)_4$, CH_2Cl_2, rt



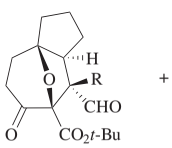
(90)

68

C_{12-13}

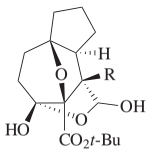


$Rh_2(OAc)_4$, CH_2Cl_2, rt



I

+

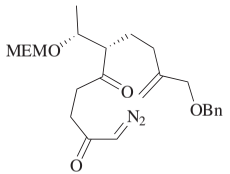
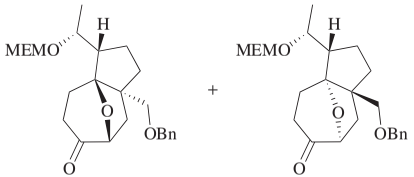


II

R	**I + II**	**I/II**
H	(85)	4:1
Me	(77)	1:1

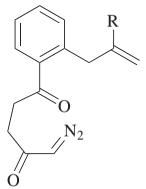
121, 122

TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

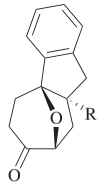
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	Catalyst, rt	 **I** **II**	

Catalyst	Solvent	I + II	I/II	
$Rh_2(OAc)_4$	CH_2Cl_2	(61)	1:1.3	70
$Rh_2(OAc)_4$	C_6H_6	(66)	1:1.25	70, 71
$Rh_2(OAc)_4$	$PhCF_3$	(45)	1:1.2	70
$Rh_2(cap)_4$	CH_2Cl_2	(25)	1:1.2	70
$Rh_2(cap)_4$	C_6H_6	(69)	1:1.1	71
$Rh_2(tfa)_4$	CH_2Cl_2	(61)	1:1.9	70
$Rh_2(tfa)_4$	$PhCF_3$	(32)	1:1.2	70
(*S*)-**6**	CH_2Cl_2	(17)	1:1.5	70
(*S*)-**6**	CH_2Cl_2	(13)	1:1.3	70
7	CH_2Cl_2	(—)	—	70
(*R*)-**10b**	CH_2Cl_2	(53)	1:1.3	70
10b	CH_2Cl_2	(62)	1:1.7	70
10b	$PhCF_3$	(35)	1:1.3	70
21	CH_2Cl_2	(54)	1:1.6	70
9c	CH_2Cl_2	(67)	1.3:1	70
9c	$PhCF_3$	(51)	1.4:1	70

C_{14-15}

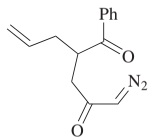


$Rh_2(OAc)_4$, C_6H_6, rt

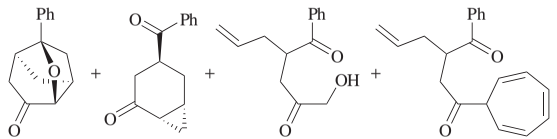


R		
H	(98)	290
Me	(88)	

C_{14}

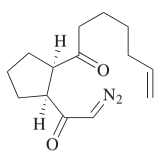


Catalyst, rt

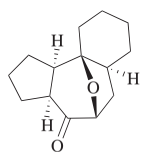


I **II** **III** **IV**

Catalyst	Solvent		I/II/III	I/II/IV	
$Rh_2(OAc)_4$	CH_2Cl_2	(70)	40:30:0	—	54
$Rh_2(OAc)_4$	C_6H_6	(76)	—	38:38:0	64
$Rh_2(cap)_4$	CH_2Cl_2	(99)	55:44:0	—	54
$Rh_2(cap)_4$	C_6H_6	(75)	—	43:32:0	64
$Rh_2(pfb)_4$	CH_2Cl_2	(59)	0:20:39	—	54
$Rh_2(tfa)_4$	CH_2Cl_2	(85)	0:35:50	—	54
$Rh_2(tfa)_4$	C_6H_6	(80)	—	0:0:80	54, 64
$Cu(acac)_2$	CH_2Cl_2	(94)	52:42:0	—	54
$PdCl_2(PhCN)_2$	CH_2Cl_2	(46)	0:46:0	—	54

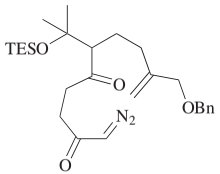
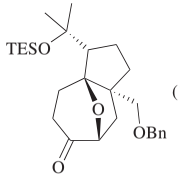
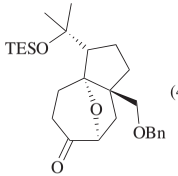
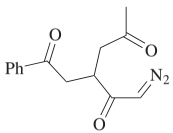
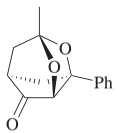
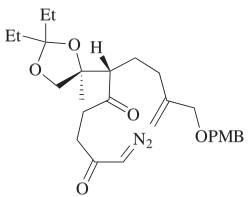
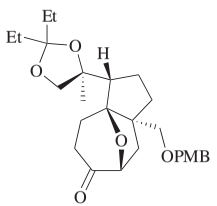
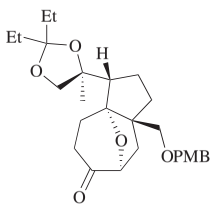


$Rh_2(OAc)_4$, CH_2Cl_2, rt



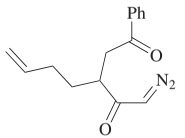
(55) 117

TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

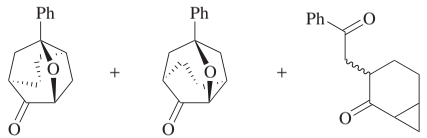
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	$Rh_2(OAc)_4$, CH_2Cl_2, 0°	 (10) +  (49)	70
	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (95)	54
	Catalyst, 4 Å MS	 +  **I** **II**	

Catalyst	Solvent	Temp (°)	**I + II**	**I/II**	Refs.
$Rh_2(OAc)_4$	CH_2Cl_2	0	(61)	1:3	74, 76
10b	CH_2Cl_2	0	(60)	1:4	76
9c	CH_2Cl_2	0	(59)	1:1.4	76
9c	$PhCF_3$	0	(54)	1.1:1	76
9c	$PhCF_3$	−40	(82)	1.6:1	74, 76

C_{15}

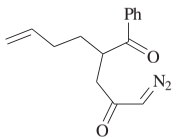


Catalyst, CH_2Cl_2, rt



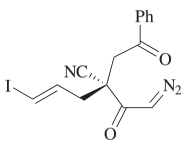
I **II** **III**

Catalyst		I/II/III	
$Rh_2(OAc)_4$	(85)	65:9:11	54
$Rh_2(OAc)_4$	(84)	60:11:13	64
$Rh_2(tfa)_4$	(67)	67:0:0	64
$Rh_2(cap)_4$	(98)	70:11:17	64

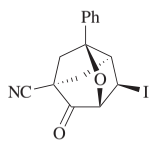


Catalyst, CH_2Cl_2, rt

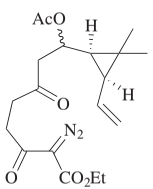
Catalyst		
$Rh_2(OAc)_4$	(82)	54, 64
$Rh_2(tfa)_4$	(78)	
$Rh_2(cap)_4$	(66)	



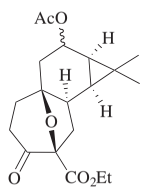
$Rh_2(OAc)_4$, CH_2Cl_2, rt



(65) 69

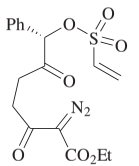
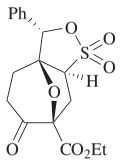
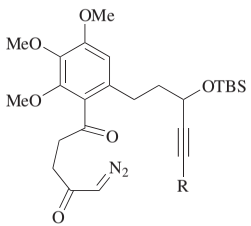
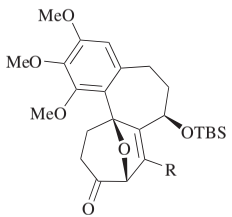
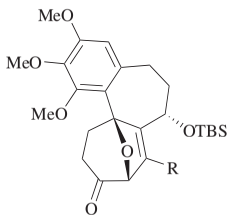
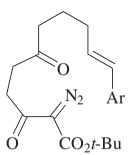
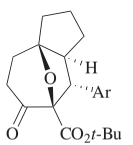


$Rh_2(OAc)_4$, toluene, 100°

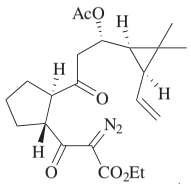


(72–75) 78

TABLE 2. INTRAMOLECULAR CYCLOADDITIONS OF NON-AROMATIC 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	$Rh_2(oct)_4$, CH_2Cl_2, 0°	 (81) dr 9.4:1	68
C_{16} 	$Rh_2(OAc)_4$, reflux	 **I** +  **II**	
		R Solvent **I + II** **I/II** H toluene (64) — TMS C_6H_6 (25) 14:1 TMS toluene (62) 14:1	82 81 81
C_{17-18} 	$Rh_2(OAc)_4$, CH_2Cl_2, rt		121, 122
		Ar (*E*)/(*Z*) Ph 100:0 (84) 4-FC_6H_4 96:4 (88) 2-ClC_6H_4 96:4 (78) 4-ClC_6H_4 100:0 (82) 4-$O_2NC_6H_4$ 100:0 (100) 4-$MeOC_6H_4$ 100:0 (100) 4-MeC_6H_4 94:6 (86)	

C_{18}



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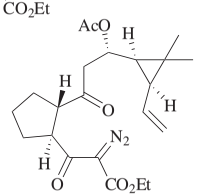
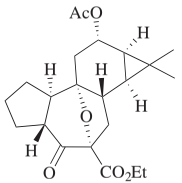
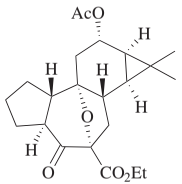


$Rh_2(OAc)_4$, toluene, 100°



I

+

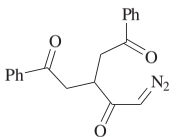


II

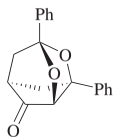
I + **II** (86), **I**/**II** = 1:1

78

C_{19}



$Rh_2(OAc)_4$, CH_2Cl_2, rt



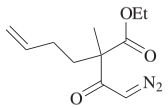
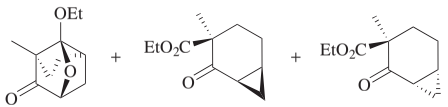
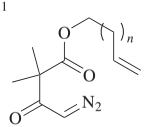
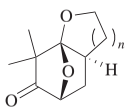
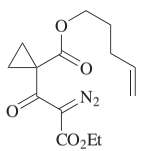
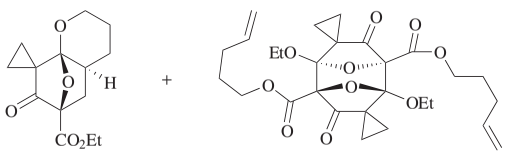
(93)

54

[a] The commercially available DOSP catalyst contains a mixture of C_{11}–C_{13} alkyl chains.

[b] The catalyst Rh_2[(*S*)-DOSP]$_4$ **10b**, containing isomerically pure dodecyl groups, was used.

TABLE 3. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED RING CARBONYL YLIDES FROM ESTERS

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	Catalyst	 **I** + **II** + **III** Catalyst / Solvent / Temp / **I** / **II** / **III** $Pd_2Cl_2(C_3H_5)_2$ / C_6H_6 / 5–10° / (3.5) / (26) / (17) $Rh_2(OAc)_4$ / Et_2O / rt / (43) / (—)[a] / (—)[a]	60
C_{10-11} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 *n* / (56) / (62) 1 / 2	204
C_{12} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 **I** + **II** Time (h) / **I** / **II** 1 / (42) / (42) 5 / (60) / (—)	155, 157

[a] The sum of the yields for products **II** and **III** is 26%.

TABLE 4. INTRAMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES (PYRYLIUMS) FROM ESTERS

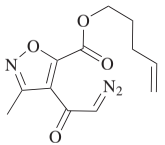
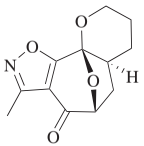
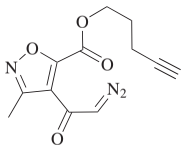
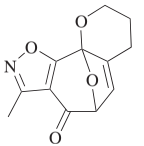
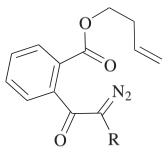
Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*			
C_{12} 	$Rh_2(OAc)_4$, toluene, 110°	 (84)	114
	$Rh_2(OAc)_4$, toluene, 110°	 (45)	114

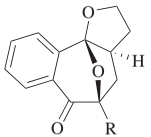
TABLE 4. INTRAMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES (PYRYLIUMS) FROM ESTERS (*Continued*)

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

$C_{13–19}$

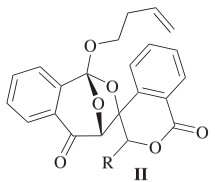


Catalyst



I

+

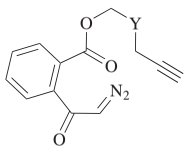


II

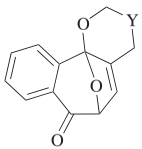
R	Catalyst	Solvent	Temp	**I**	er	**II**	
H	$Rh_2(OAc)_4$	C_6H_6	rt	(87)	—	(10)	208, 209
H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(78)	—	(—)	207
H	(*R*)-**6**	CH_2Cl_2	rt	(60)	50.0:50.0	(—)	207
H	**18**	CH_2Cl_2	rt	(73)	50.0:50.0	(—)	207
H	**4**	CH_2Cl_2	rt	(80)	50.0:50.0	(—)	207
H	**8a**	CH_2Cl_2	rt	(79)	50.0:50.0	(—)	207
H	**10b**	CH_2Cl_2	rt	(85)	53.0:47.0	(—)	207
H	(*R*)-**6**	hexane	rt	(9)	—	(—)	207
H	**18**	hexane	rt	(16)	—	(—)	207
H	**4**	hexane	rt	(30)	—	(—)	207
H	**8a**	hexane	rt	(43)	—	(—)	207
H	**10b**	hexane	rt	(32)	55.5:44.5	(—)	207
H	(*R*)-**6**	C_6H_6	rt	(31)	51.0:49.0	(—)	207
H	**18**	C_6H_6	rt	(50)	52.5:47.5	(—)	207
H	**4**	C_6H_6	rt	(93)	52.0:48.0	(—)	207
H	**8a**	C_6H_6	rt	(95)	54.5:45.5	(—)	207
H	**10b**	C_6H_6	rt	(96)	58.0:42.0	(—)	207
H	(*R*)-**6**	C_6H_6	40°	(64)	53.5:46.5	(—)	207
H	**18**	C_6H_6	40°	(65)	53.5:46.5	(—)	207

H	**4**	C_6H_6	40°	(93)	51.0:49.0	(—)	207
H	**8a**	C_6H_6	40°	(95)	51.0:49.0	(—)	207
H	**10b**	C_6H_6	40°	(90)	53.5:46.5	(—)	207
H	(*R*)-**6**	C_6H_6	7°	(23)	52.0:48.0	(—)	207
H	**18**	C_6H_6	7°	(44)	57.5:42.5	(—)	207
H	**4**	C_6H_6	7°	(50)	51.5:48.5	(—)	207
H	**8a**	C_6H_6	7°	(70)	51.0:49.0	(—)	207
H	**10b**	C_6H_6	7°	(76)	59.5:40.5	(—)	207
Ph	$Rh_2(OAc)_4$	toluene	110°	(96)	—	(0)	119

C_{13-14}

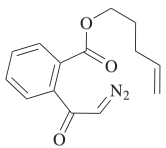
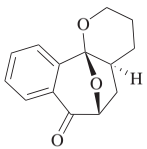
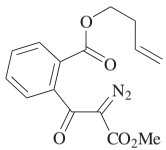
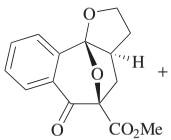
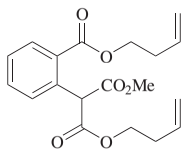
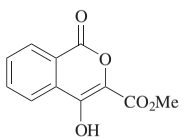


$Rh_2(OAc)_4$



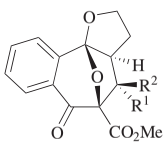
Y	Solvent	Temp		
O	CH_2Cl_2	rt	(74)	125
CH_2	—	—	(68)	130

TABLE 4. INTRAMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES (PYRYLIUMS) FROM ESTERS (*Continued*)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	$Rh_2(OAc)_4$	 (—)	130
	Catalyst, rt	 +  +  **I** **II** **III**	207

Catalyst	Solvent	I	er	II	III
10b	hexane	(88)	51.0:49.0	(0)	(0)
10b	CH_2Cl_2	(78)	53.0:47.0	(0)	(0)
10b	C_6H_6	(82)	53.0:47.0	(0)	(0)
18	hexane	(0)	—	(25)	(26)
18	CH_2Cl_2	(41)	50.0:50.0	(0)	(31)
18	C_6H_6	(79)	50.0:50.0	(0)	(0)

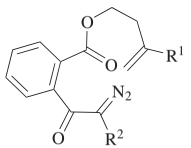
1.  ,
Grubbs' 2nd-gen Ru cat. (5 mol %), CH_2Cl_2, reflux
2. $Rh_2(OAc)_4$, CH_2Cl_2, rt



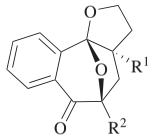
R^1	R^2	R^3	
MeO_2C	H	H	(68)
Ph	H	H	(86)
Me	Me	Me	(83)
CHO	Me	H	(54)

122

C_{14-19}

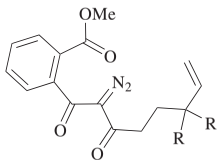


$Rh_2(OAc)_4$

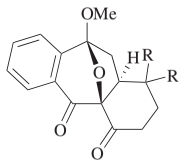


R^1	R^2	Solvent	Temp		
Me	H	C_6H_6	rt	(80)	208, 209
H	Ph	toluene	110°	(96)	119

C_{15-17}

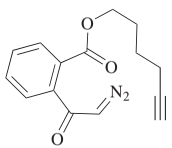


$Rh_2(OAc)_4$, C_6H_6, 80°

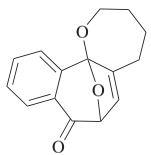


R		
H	(75)[a]	205, 206
Me	(92)[b]	

C_{15}

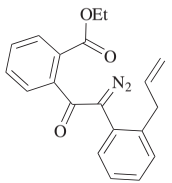
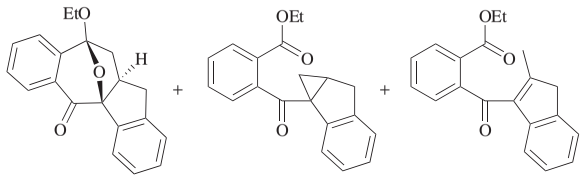


$Rh_2(OAc)_4$

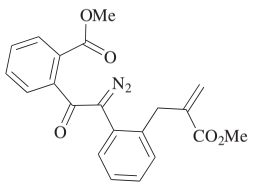
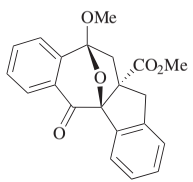


(25) 130

TABLE 4. INTRAMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES (PYRYLIUMS) FROM ESTERS (*Continued*)

Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	Catalyst	 **I** + **II** + **III**	119

Catalyst	Solvent	Temp (°)	**I**	**II + III**	**I/(II + III)**
$Rh_2(OAc)_4$	hexane	80	(65)	(20)	—
$Rh_2(tfa)_4$	toluene	110	(87)	(—)	>10:1

C_{19} 	$Rh_2(OAc)_4$, hexane, 80°	 (68)	119

[a] The yield was 25% on the basis of the weight of isolated cycloadduct described in the experimental sections.

[b] The yield was 33% on the basis of the weight of isolated cycloadduct described in the experimental sections.

TABLE 5. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM AMIDES

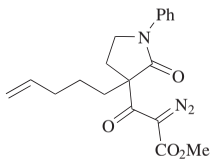
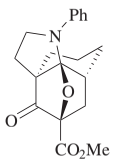
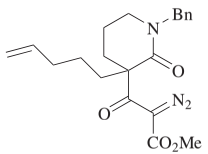
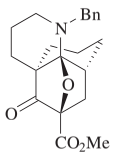
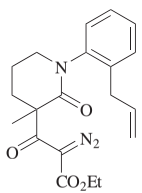
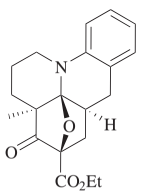
Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 (85)	118
C_{13} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 (87)	118
C_{18} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 (87)	118

TABLE 6. INTRAMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES (PYRYLIUMS) FROM AMIDES

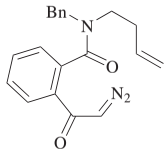
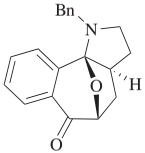
Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	$Rh_2(OAc)_4$, C_6H_6, rt	 (87)	208, 209

TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES

A. NON-AROMATIC YLIDES

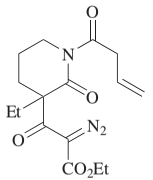
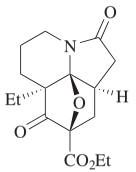
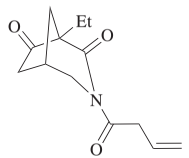
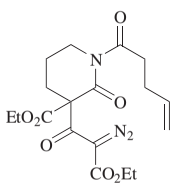
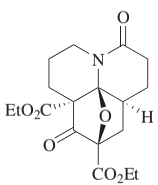
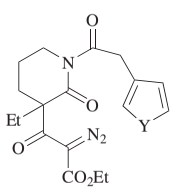
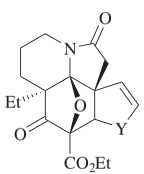
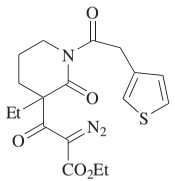
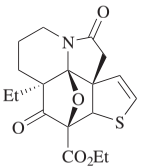
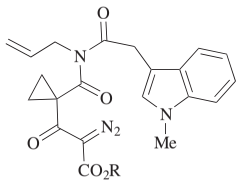
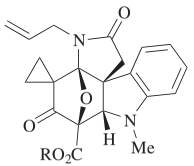
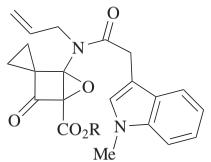
Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*			
C_{14} 	Catalyst, 90°	 **I** +  **II** Catalyst **I** **II**: $Rh_2(Opiv)_4$ (98) (0); $Rh_2(cap)_4$ (98) (0); $Rh_2(OAc)_4$ (91) (4); $Rh_2(man)_4$ (88) (6); $Rh_2(tfa)_4$ (73) (22); $Rh_2(pfb)_4$ (62) (32)	134, 135
	$Rh_2(OAc)_4$, C_6H_6, 50°	 (95)	214
C_{16} 	1. $Rh_2(Opiv)_4$, 4 Å MS, 100°, 10 min 2. Diazo substrate, C_6H_6, 90°; microwave (140 W), 40 min	 Y: O (35); S (38)	131, 134

TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

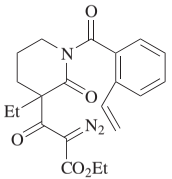
A. NON-AROMATIC YLIDES (*Continued*)

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	$Rh_2(Opiv)_4$, C_6H_6, 90°	 (35)	135
C_{17} 	Catalyst	 + 	142

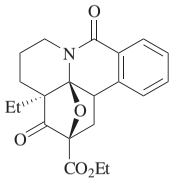
I **II**

R	Catalyst	Solvent	Temp (°)	**I**	er	**II**
Me	**8f**	$PhCF_3$	60	(42)	68.5:31.5	(42)
t-Bu	**8f**	$PhCF_3$	60	(66)	60.0:40.0	(trace)
Bn	**8f**	$PhCF_3$	60	(50)	81.5:18.5	(27)
$PhCH_2CH_2$	**8f**	$PhCF_3$	60	(48)	68.0:32.0	(37)
Bn	**8e**	$PhCF_3$	60	(42)	76.5:23.5	(4)
Bn	**8d**	$PhCF_3$	60	(55)	61.0:39.0	(16)
Bn	**8f**	toluene	60	(44)	80.0:20.0	(21)
Bn	**8f**	CH_2Cl_2	60	(42)	72.0:28.0	(17)
Bn	**8f**	$PhCF_3$	40	(43)	83.0:17.0	(34)
Bn	**8f**	$PhCF_3$	80	(50)	78.5:21.5	(23)

C_{19}

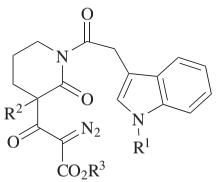


$Rh_2(OAc)_4$, C_6H_6, rt

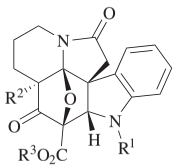


(95) 131, 134

$C_{19–20}$

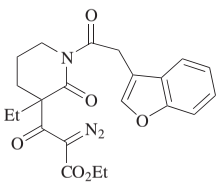


$Rh_2(OAc)_4$, C_6H_6

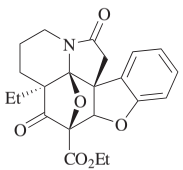


R^1	R^2	R^3	Temp (°)		
Me	EtO_2C	Et	50	(90)	118, 138
Me	Et	Me	50	(95)	118, 131, 134, 138, 213
Me	$BnOCH_2CH_2$	Me	80	(96)	138
PhO_2S	$BnOCH_2CH_2$	Et	80	(90)	138
PhO_2S	$BnOCH_2CH_2$	Et	80	(94)	215
Ts	MeO_2CCH_2	Me	80	(98)	137, 138
Ts	$BnOCH_2CH_2$	Me	80	(90)	137, 138, 215

C_{20}



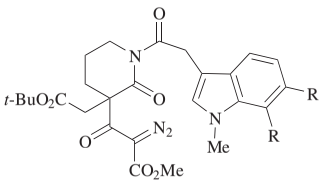
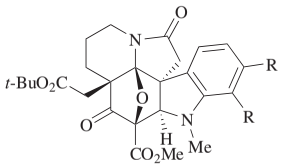
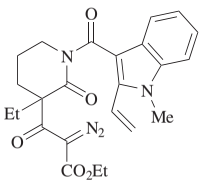
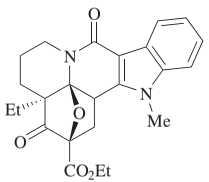
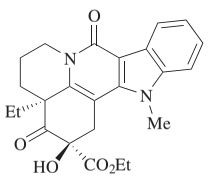
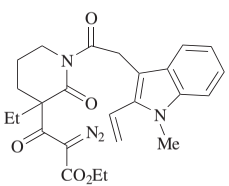
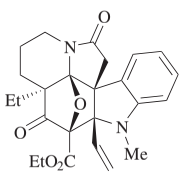
1. $Rh_2(Opiv)_4$, 4 Å MS, 100°, 10 min
2. Diazo compound, C_6H_6, 70°; microwave (120 W), 2 h

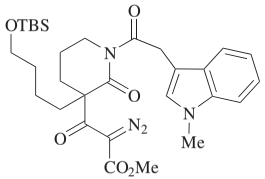


(90) 131, 134

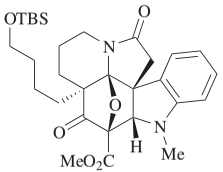
TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

	Imide	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{20}		$Rh_2(OAc)_4$, C_6H_6, 100°		(97) R = H; MeO	138, 139, 141; 139, 141, 215
C_{21}		$Rh_2(OAc)_4$, C_6H_6, rt		(92)	131, 134
		$Rh_2(OAc)_4$, C_6H_6, >50°		(90)	131, 134
C_{22}		$Rh_2(OAc)_4$, toluene, microwave (125 W), 100°		(95)	131, 134



$Rh_2(oct)_4$, C_6H_6, 50°



(74)

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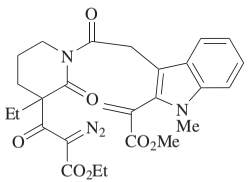
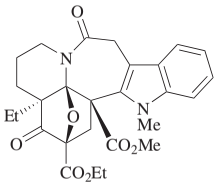
C_{23}



1. $Rh_2(Opiv)_4$, 4 Å MS, 100°, 10 min
2. Diazo substrate, C_6H_6, 90°, microwave (150 W), 2 h

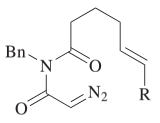
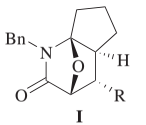
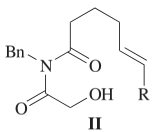
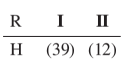
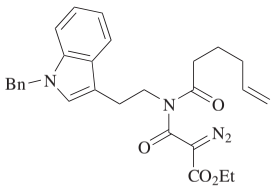
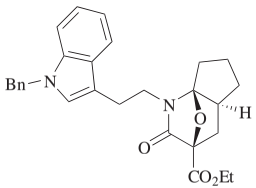
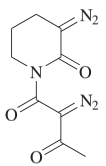
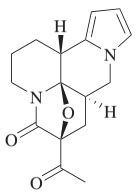


(91)

134

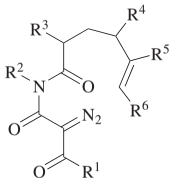
TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES

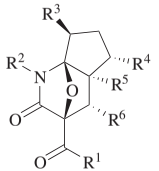
Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 	$Rh_2(OAc)_4$, toluene, 110°	 **I** +  **II** 	72
C_9 	$Rh_2(pfb)_4$, C_6H_6, 80°	 (98)	79
	$Rh_2(OAc)_4$, CH_2Cl_2, rt, *N*-allylpyrrole, then solvent exchange to C_6H_6, reflux	 (85)	143

R	**I**	**II**
H	(39)	(12)
Me	(27)	(31)

C_{10-16}



Catalyst



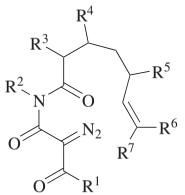
R^1	R^2	R^3	R^4	R^5	R^6	Catalyst	Solvent	Temp		
Me	Bn	H	H	H	H	$Rh_2(OAc)_4$	toluene	110°	(91)	72
MeO	Bn	H	H	H	Me	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(78)	66
Me	Bn	H	H	H	Me	$Rh_2(OAc)_4$	toluene	110°	(74)	72
EtO	3,4-$(MeO)_2C_6H_3CH_2CH_2$	H	H	Me	H	$Rh_2(pfb)_4$	toluene	110°	(95)	79
EtO	3,4-$(MeO)_2C_6H_3CH_2CH_2$	Me	H	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(90)	79
Me	Bn	Me	H	H	Me	$Rh_2(OAc)_4$	toluene	110°	(73)	72
EtO	Bn	H	3-$MeOC_6H_4CH_2$	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(89)	73
EtO	Bn	H	3,4-$(MeO)_2C_6H_3CH_2$	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(80)	73

TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

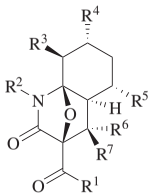
B. ISOMÜNCHNONES (*Continued*)

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

$C_{10–17}$

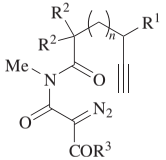


Catalyst

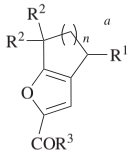


R^1	R^2	R^3	R^4	R^5	R^6	R^7	Catalyst	Solvent	Temp		
EtO	2-$IC_6H_4CH_2CH_2$	H	H	H	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(86)	77
EtO	3,4-$(MeO)_2C_6H_3CH_2CH_2$	H	H	H	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(98)	79
EtO	$TsCH_2CH_2$	H	H	H	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(85)	77
Me	Me	H	H	H	H	H	$Rh_2(OAc)_4$	C_6H_6	80°	(71)	66
EtO	Bn	H	Me	H	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(90)	77
EtO	$TsCH_2CH_2$	H	Me	H	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(85)	77
EtO	Bn	H	Me	H	Me	Me	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(90)	77
Me	Bn	H	H	H	H	Me	$Rh_2(OAc)_4$	toluene	110°	(72)	72
Me	Bn	Me	H	H	H	Me	$Rh_2(OAc)_4$	toluene	110°	(75)	72
EtO	3-methylbut-3-en-1-yl	H	Me	H	Me	Me	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(94)	77, 79
EtO	Bn	H	H	3-$MeOC_6H_4CH_2$	H	H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(95)	73

C_{11-13}

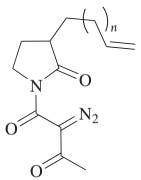


$Rh_2(OAc)_4$, toluene, 110°

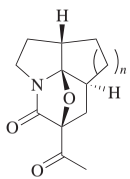


n	R^1	R^2	R^3		
1	H	H	Me	(44)	128
2	H	H	Me	(52)	
2	H	Me	MeO	(49)	
2	BzO	H	MeO	(60)	
2	BzO	H	Me	(63)	

C_{12-13}

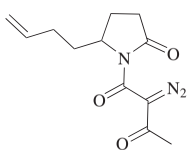


$Rh_2(OAc)_4$, C_6H_6, 80°

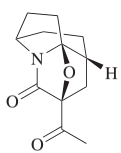


n		
1	(88)	61, 66
2	(71)	66

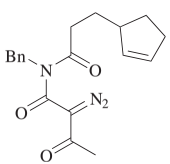
C_{12}



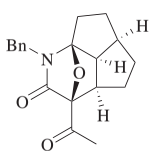
$Rh_2(OAc)_4$, C_6H_6, 80°



(69) 61, 66



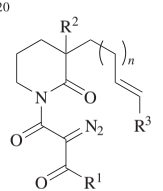
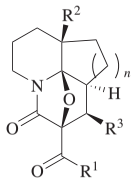
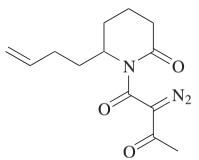
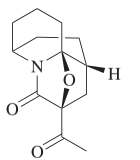
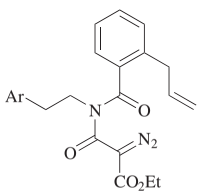
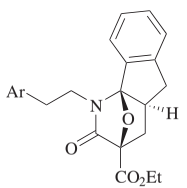
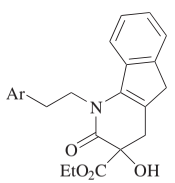
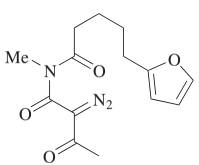
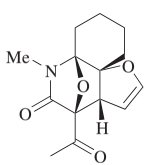
$Rh_2(OAc)_4$, toluene, 110°



(79) 72

TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-20} 	Catalyst, C_6H_6, 80°		61, 66, 212, 66
C_{13} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 (76)	61, 66
 Ar = 3,4-$(MeO)_2C_6H_3$	$Rh_2(pfb)_4$, CH_2Cl_2, rt	 **I** +  **II** **I** + **II** (75), **I**/**II** = 4:1	79
	$Rh_2(OAc)_4$, C_6H_6, 80°	 (74)	132, 133

n	R^1	R^2	R^3	Catalyst		
1	Me	H	H	$Rh_2(OAc)_4$	(86)	61, 66
1	EtO	Et	2-$O_2NC_6H_4$	$Rh(pfb)_4$	(85)	212
2	Me	H	H	$Rh_2(OAc)_4$	(86)	66

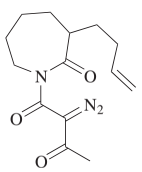
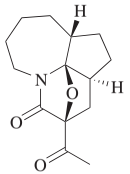
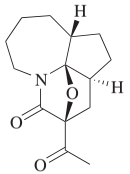
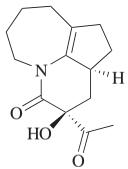
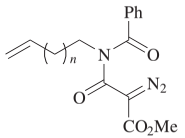
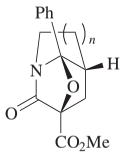
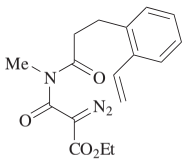
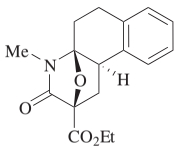
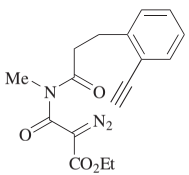
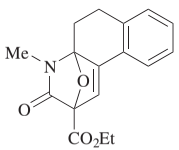
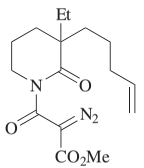
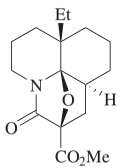
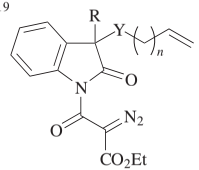
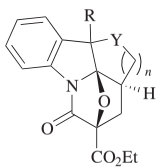
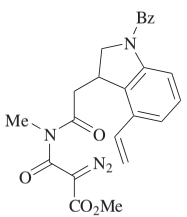
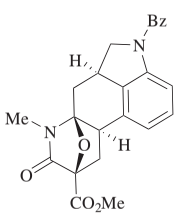
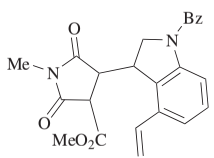
C_{14} 	$Rh_2(OAc)_4$, C_6H_6, 80°		(83)			61
	1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. Chromatography on SiO_2		(40)	+		(36)	66
C_{14-15} 	$Rh_2(tfa)_4$, C_6H_6, 80°		n 1 (100) 1 (>95) 2 (98)			211 210 210, 211
C_{14} 	$Rh_2(pfb)_4$, CH_2Cl_2, rt		(75)			129
	$Rh_2(pfb)_4$, CH_2Cl_2, reflux		(80)			129

TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	$Rh_2(pfb)_4$, C_6H_6, 80°	 (97)	212
C_{15-19} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 *n* R Y 1 TBSO CH_2 (70) 1 Me O (72) 1 pent-4-en-1-yl O (75) 2 TBSO CH_2 (69) 2 Me O (82) 3 Me O (80)	164
C_{15} 	Catalyst	 +  **I** **II** Catalyst Solvent Temp Time (h) **I** **II** $Rh_2(OAc)_4$ C_6H_6 50° 12 (67) (33) $Rh_2(pfb)_4$ CH_2Cl_2 rt 2 (93) (—)	129

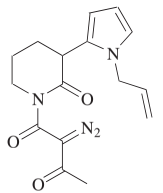
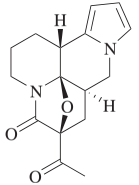
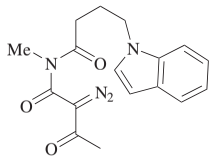
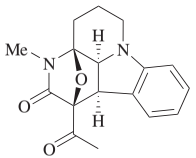
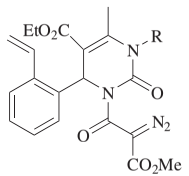
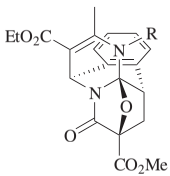
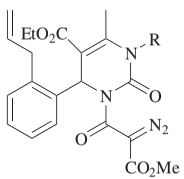
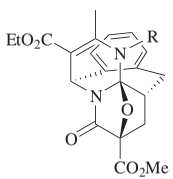
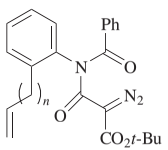
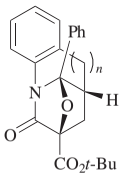
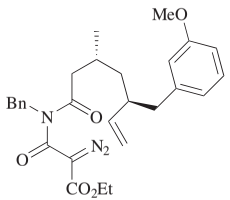
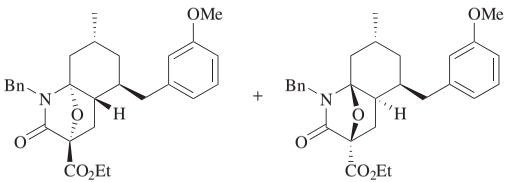
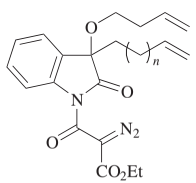
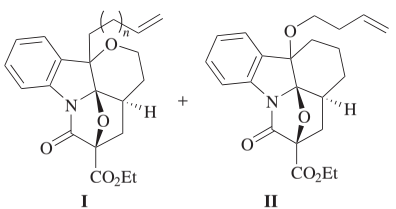
C_{16}		$Rh_2(OAc)_4$, C_6H_6, reflux		(90)	143
		$Rh_2(OAc)_4$, C_6H_6, 80°		(75)	133
C_{17}		$Rh_2(OAc)_4$, C_6H_6, 80°		R Me (92) Cbz (71) Bn (58)	63 62 62
C_{18}		$Rh_2(OAc)_4$, C_6H_6, 80°		R Me (88) Cbz (56)	63 62

TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

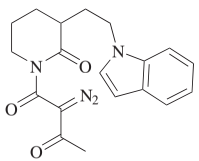
B. ISOMÜNCHNONES (*Continued*)

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18-19} 	$Rh_2(OAc)_4$, C_6H_6, 80°		210, 211
C_{18} 	$Rh_2(pfb)_4$, CH_2Cl_2, rt	 **I** **I** + **II** (97), **I**/**II** = 3:2 **II**	73
C_{19-20} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 **I** **II**	164

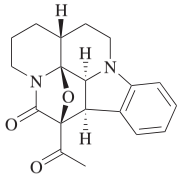
n		
0	(93)	
1	(95)	

n	**I**	**II**
1	(79)	(0)
2	(55)	(11)

C_{19}



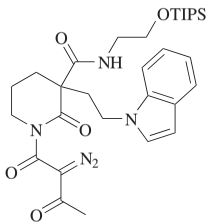
$Rh_2(OAc)_4$, C_6H_6, 80°



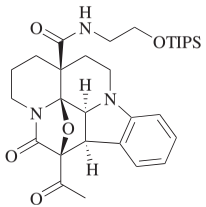
(67)

61, 133

C_{20}

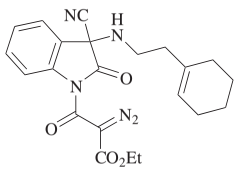


$Rh_2(oct)_4$, C_6H_6, 50°

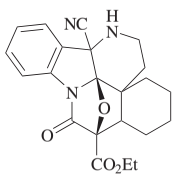


(73)

136



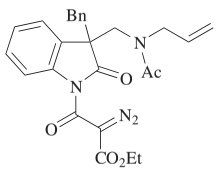
$Rh_2(OAc)_4$, C_6H_6, 80°



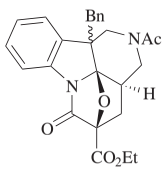
(83) dr 8:5

345

C_{22}



$Rh_2(OAc)_4$, C_6H_6, 80°

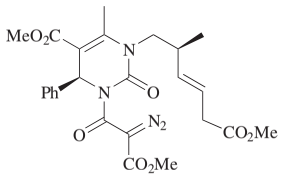
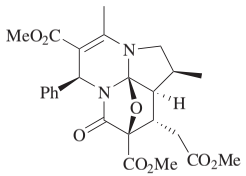
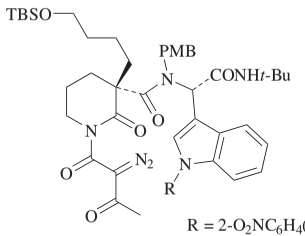
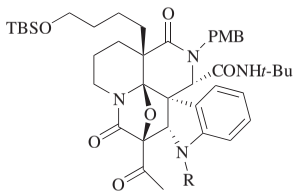


(89) dr 2:1

345

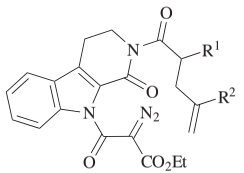
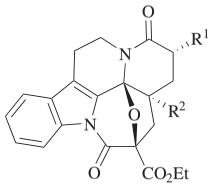
TABLE 7. INTRAMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	$Rh_2(OAc)_4$, C_6H_6, 80°	 (80)	75
C_{24}  R = 2-$O_2NC_6H_4(O_2)S$	$Rh_2(oct)_4$, C_6H_6, 50°	 (57)	136

[a] The product results from expulsion of methyl isocyanate from the intermediate cycloadduct.

TABLE 8. INTRAMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM IMIDES

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{19–21}$ 	$Rh_2(OAc)_4$, C_6H_6		80, 80, 139, 80

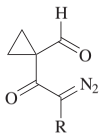
R^1	R^2	Temp (°)		
H	H	80	(95)	80
H	Et	100	(95)	80, 139
Et	H	80	(90)	80

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES

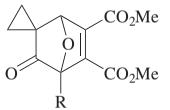
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.

See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*

C_{6-7}

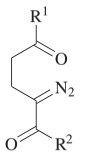


$Rh_2(OAc)_4$

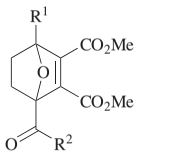


R	Solvent	Temp		
H	$CHCl_3$	rt	$(97)^a$	112, 113
EtO_2C	C_6H_6	80°	(97)	155

C_{7-17}

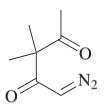


$Rh_2(OAc)_4$, CH_2Cl_2, rt

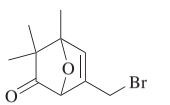


R^1	R^2		
Me	Me	(76)	
Ph	EtO	(91)	120
Ph	Me	(88)	
Ph	Ph	(90)	
Me	Ph	(78)	

C_7

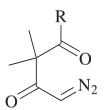


$Rh_2(OAc)_4$, rt

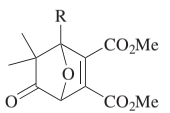


Solvent		
CH_2Cl_2	(66)	190
$[bmim]BF_4$	(72)	

C_{7-12}

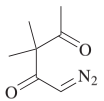


Catalyst

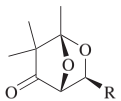


R	Catalyst	Solvent	Temp		er	
Me	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(85)	—	190
Me	$Rh_2(OAc)_4$	$[bmim]BF_4$	rt	(92)	—	190
i-Pr	$Rh_2(OAc)_4$	—	rt	(63)	—	113
Ph	**9c**	$PhCF_3$	–23°	(75)	84.0:16.0	97

C_7

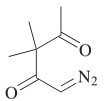
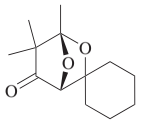
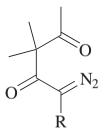
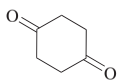
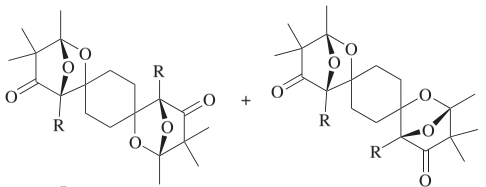


Catalyst

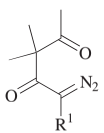


R	Catalyst	Solvent	Temp		er	
(*E*)-MeCH=CH	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(64)	—	176
2-furyl	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(66)	—	176
$4\text{-}O_2NC_6H_4$	**9c**	$PhCF_3$	0°	(74)	56.0:44.0	99
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(79)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[bmim]BF_4$	rt	(84)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(oct)_4$	$[bmim]BF_4$	rt	(86)	—	190
$4\text{-}MeOC_6H_4$	$Cu(acac)_2$	$[bmim]BF_4$	80°	(66)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[bbim]BF_4$	rt	(82)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(oct)_4$	$[bbim]BF_4$	rt	(85)	—	190
$4\text{-}MeOC_6H_4$	$Cu(acac)_2$	$[bbim]BF_4$	80°	(62)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[bbim]PF_6$	rt	(55)	—	190
$4\text{-}MeOC_6H_4$	$Cu(acac)_2$	$[bmim]PF_6$	80°	(35)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[mmim]BF_4$	rt	(88)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(oct)_4$	$[mmim]BF_4$	rt	(90)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[bmim]BF_4$, 2nd cycle[b]	rt	(88)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[bmim]BF_4$, 3rd cycle[b]	rt	(85)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[bmim]BF_4$, 4th cycle[b]	rt	(86)	—	190
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	$[bmim]BF_4$, 5th cycle[b]	rt	(85)	—	190
(*E*)-PhCH=CH	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(73)	—	176
9-anthryl	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(85)	—	190
9-anthryl	$Rh_2(OAc)_4$	$[bmim]BF_4$	rt	(91)	—	190
1-pyrenyl	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(89)	—	190
1-pyrenyl	$Rh_2(OAc)_4$	$[bmim]BF_4$	rt	(97)	—	190

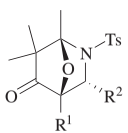
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (35)	179
C_{7-8} 		$Rh_2(OAc)_4$	 **I** **II**	188

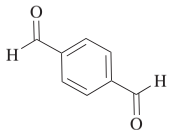
R	Solvent	Temp	**I**	**II**
H	CH_2Cl_2	rt	(23)	(45)
EtO_2C	C_6H_6	80°	(78)	(0)



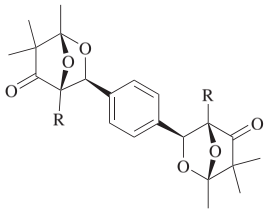
$Rh_2(OAc)_4$



R^1	R^2	Solvent	Temp		Refs.
H	Ph	CH_2Cl_2	rt	(74)	196, 303
H	3-FC_6H_4	CH_2Cl_2	rt	(66)	196, 303
H	4-FC_6H_4	CH_2Cl_2	rt	(64)	196, 303
H	3-BrC_6H_4	CH_2Cl_2	rt	(60)	196, 303
H	2-ClC_6H_4	CH_2Cl_2	rt	(74)	303
H	2-BrC_6H_4	CH_2Cl_2	rt	(81)	303
H	4-MeC_6H_4	CH_2Cl_2	rt	(62)	196, 303
EtO_2C	Ph	C_6H_6	80°	(57)	196

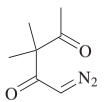


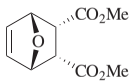
$Rh_2(OAc)_4$



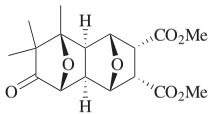
R	Solvent	Temp		
H	CH_2Cl_2	rt	(82)	193
EtO_2C	C_6H_6	80°	(64)	

C_7



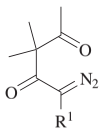


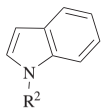
$Rh_2(OAc)_4$, CH_2Cl_2, rt



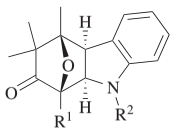
(82) 293

C_{7-8}



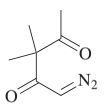
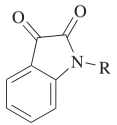
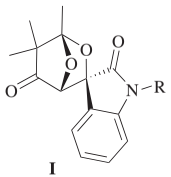
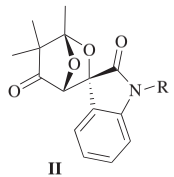


Catalyst

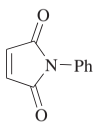
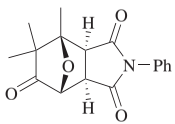


R^1	R^2	Catalyst	Solvent	Temp	er		
H	H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	—	(86)	161
H	Me	$Rh_2(OAc)_4$	CH_2Cl_2	rt	—	(89)	161
H	Bn	$Rh_2(OAc)_4$	CH_2Cl_2	rt	—	(87)	161
t-BuO_2C	Me	**8f**	$PhCF_3$	rt	75.0:25.0	(40)[c]	346
t-BuO_2C	Me	**8f**	$PhCH_3$	60°	80.5:19.5	(84)	346
t-BuO_2C	Me	**8f**	$PhCF_3$	80°	79.5:20.5	(80)	346

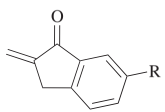
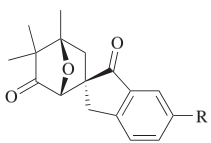
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** +  **II**	179

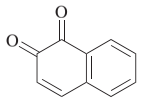
R	**I**	dr	**II**	dr
H	(62)	—	(22)	—
Me	(50)	—	(36)	—
Bn	(49)	—	(35)	—
EtO_2CCH_2	(68)	—	(26)	—
$EtO_2C(CH_3)CH$	(45)	1:2.6	(33)	1:1.3

		$Rh_2(OAc)_4$, rt		190

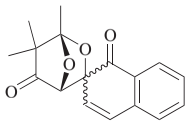
Solvent	
CH_2Cl_2	(81)
[bmim]BF_4	(87)

		$Rh_2(OAc)_4$, CH_2Cl_2, rt		169

R	
H	(92)
MeOCHN	(78)



$Rh_2(OAc)_4$, CH_2Cl_2, rt



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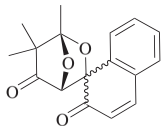

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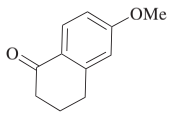
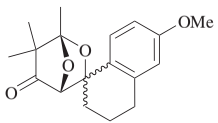
179



$Rh_2(OAc)_4$, CH_2Cl_2, rt



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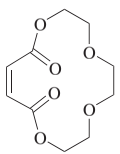
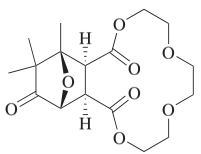
179



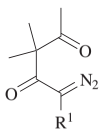
$Rh_2(OAc)_4$, CH_2Cl_2, rt

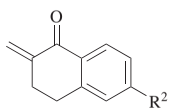


(76)

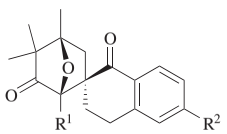
294

C_{7-8}



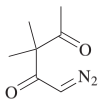
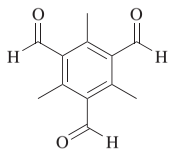
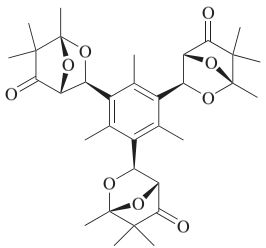
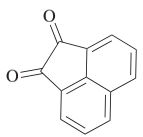
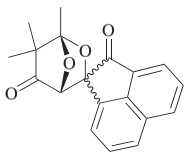
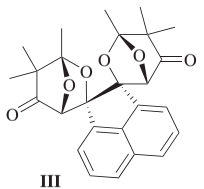
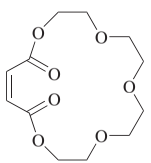
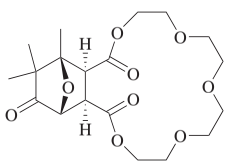


$Rh_2(OAc)_4$



R^1	R^2	Solvent	Temp		
H	H	CH_2Cl_2	rt	(81)	
H	MeO	CH_2Cl_2	rt	(75)	169
EtO_2C	H	C_6H_6	80°	(75)	
EtO_2C	MeO	C_6H_6	80°	(87)	

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (70)	193
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 +  **I + II** **III**	
			I + II **I/II** **III** (60) 60:40 (25)	188
			(75) 54:46 (—)	179
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (74)	294

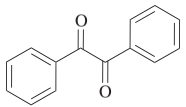
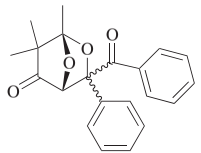
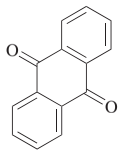
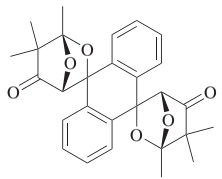
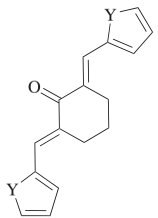
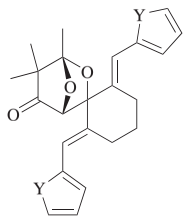
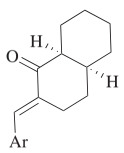
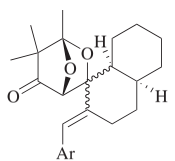
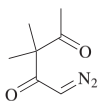
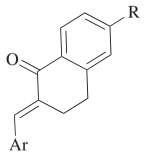
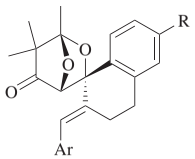
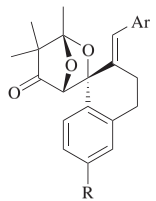
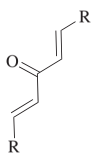
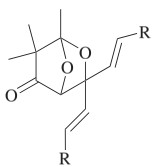
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(74) dr 1:1.5	179
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(70)	193
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		Y O (72) S (73)	178, 180
 Ar = 4-ClC_6H_4	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(55) dr 1:2	180

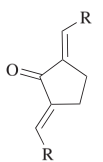
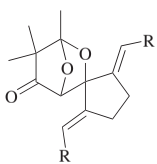
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 +  **I** **II**	180

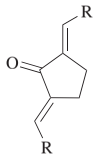
R	Ar	I	II
MeO	4-$MeOC_6H_4$	(39)	(25)
MeO	4-ClC_6H_4	(36)	(27)
H	4-MeC_6H_4	(23)	(36)

	$Rh_2(OAc)_4$, CH_2Cl_2, rt		180

R		
$MeOC_6H_4$	(75)	
MeC_6H_4	(77)	
(*E*)-PhCH=CH	(74)	

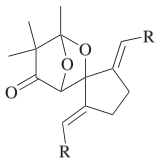
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		

R		
4-ClC_6H_4	(72)	178
4-MeC_6H_4	(71)	180
(*E*)-PhC(CH_3)=CH	(69)	180
1-naphthyl	(75)	180

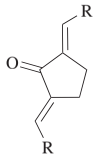


R = (*E*)-PhCH=CH

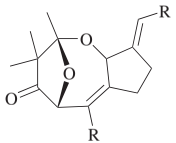
1. $Rh_2(OAc)_4$, CH_2Cl_2, rt
2. Rapid chromatography on neutral Al_2O_3



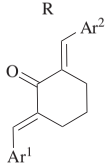
(75) 180



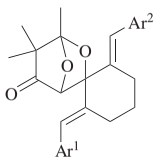
1. $Rh_2(OAc)_4$, CH_2Cl_2, rt
2. Al_2O_3 chromatography



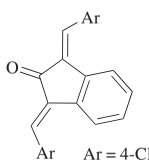
R		
(*E*)-PhCH=CH	(23)	180
(*E*)-2-$MeOC_6H_4$CH=CH	(35)	



$Rh_2(OAc)_4$, CH_2Cl_2, rt

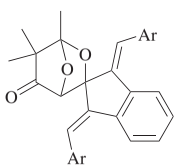


Ar^1	Ar^2		dr	
Ph	Ph	(77)	—	178
4-ClC_6H_4	4-ClC_6H_4	(71)	—	178, 180
4-$MeOC_6H_4$	4-$MeOC_6H_4$	(75)	—	178
2,4-$(MeO)_2C_6H_3$	2,4-$(MeO)_2C_6H_3$	(75)	—	178
4-MeC_6H_4	Ph	(88)	2:1	180



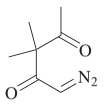
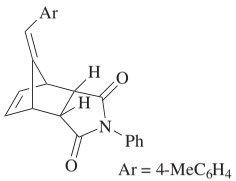
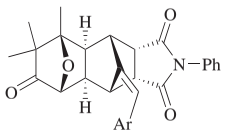
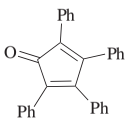
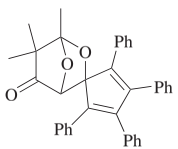
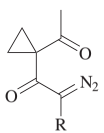
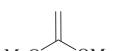
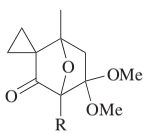
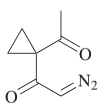
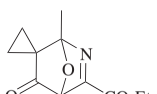
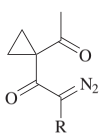
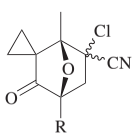
Ar = 4-ClC_6H_4

$Rh_2(OAc)_4$, CH_2Cl_2, rt



(72) 180

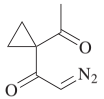
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	 Ar = 4-MeC$_6$H$_4$	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (78)	293
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (53)	176
C_{7-8} 		Catalyst, rt		58, 156
C_7 		$Rh_2(OAc)_4$, $CHCl_3$, rt	 (76)	112, 113
C_{7-8} 		Catalyst, rt		58, 156

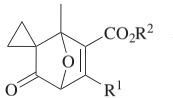
R	Catalyst	Solvent		
H	$Rh_2(oct)_4$	CH_2Cl_2	(82)	
EtO_2C	$Rh_2(OAc)_4$	C_6H_6	(81)	

R	Catalyst	Solvent		dr
H	$Rh_2(oct)_4$	CH_2Cl_2	(68)	3:1
EtO_2C	$Rh_2(OAc)_4$	C_6H_6	(60)	3:1

C_7

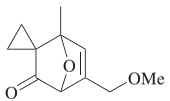


$Rh_2(OAc)_4$, rt



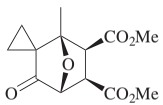
R^1	R^2	Solvent		
H	Me	$CHCl_3$	(58)	112, 113
Et	Et	CH_2Cl_2	(64)	262
$THPO(CH_2)_3$	Me	CH_2Cl_2	(21)[d]	262
$TBSO(CH_2)_3$	Me	CH_2Cl_2	(60)	262
n-Bu	Me	CH_2Cl_2	(—)	262

$Rh_2(OAc)_4$, $CHCl_3$, rt



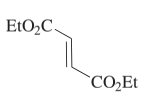
(59) 112, 113

Catalyst, C_6H_6, rt

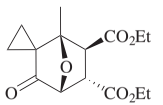


(76)

Catalyst	
$Rh_2(OAc)_4$	58
$Rh_2(oct)_4$	156

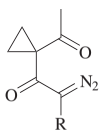


$Rh_2(OAc)_4$, C_6H_6, rt

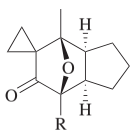


(83) 58

C_{7-8}

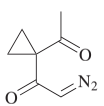


$Rh_2(OAc)_4$



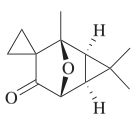
R	Solvent	Temp		
H	—	rt	(65)	58
EtO_2C	C_6H_6	80°	(71)	

C_7



x eq

$Rh_2(OAc)_4$, CH_2Cl_2, rt

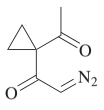


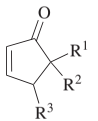
x		
3	(50)	148
5	(81)	

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

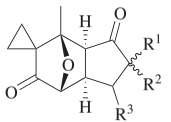
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.

C_7



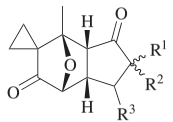


Catalyst



I

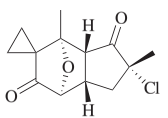
+



II

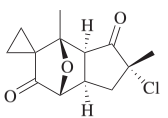
R^1	R^2	R^3	Catalyst	Solvent(s)	Temp	**I + II**	**I/II**	
H	H	H	$Rh_2(OAc)_4$	—	—	(40)	100:0	173
H	H	H	"Rh(II) catalyst"	—	—	(86)	4:1	172
H	H	H	$Rh_2(oct)_4$	CH_2Cl_2	rt	(74)	4:1	58, 156
Me	Me	H	$Rh_2(OAc)_4$	C_6H_6	rt	(80)	100:0	58
Me	Me	H	$Rh_2(oct)_4$	Et_2O	rt	(60)	—	170
Me	Me	H	$Rh_2(OAc)_4$	CH_2Cl_2, DMF	reflux	(54)	100:0	263
Me	Me	Br	$Rh_2(oct)_4$	Et_2O	rt	(86)	—	170
Me	Me	Br	$Rh_2(OAc)_4$	CH_2Cl_2, DMF	reflux	(49)	100:0	177
Me	Me	AcO	$Rh_2(oct)_4$	Et_2O	rt	(76)	—	170
Me	$AcOCH_2$	H	$Rh_2(oct)_4$	Et_2O	rt	(68)	—	170
Me	$AcOCH_2$	Br	$Rh_2(oct)_4$	Et_2O	rt	(73)	—	170
Me	$AcOCH_2$	AcO	$Rh_2(oct)_4$	Et_2O	rt	(70)	—	170

$Rh_2(OAc)_4$, DMF, CH_2Cl_2, reflux



(54)

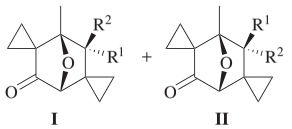
+



(20)

175

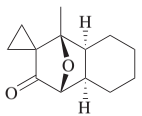
$Rh_2(OAc)_4$, CH_2Cl_2, 20°



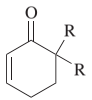
I **II**

R^1	R^2	**I**	**II**	
Ph	H	(2)	(4)	147
MeO_2C	Cl	(52)	(23)	

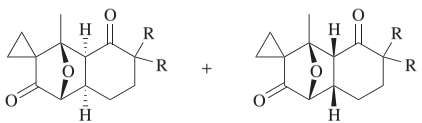
$Rh_2(OAc)_4$, rt



(16) 58



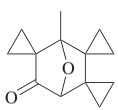
$Rh_2(oct)_4$, rt



I **II**

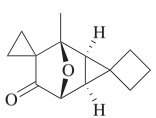
R	Solvent	**I + II**	**I/II**	
H	CH_2Cl_2	(62)	—	58
H	CH_2Cl_2	(41)	5:1	156
Me	Et_2O	(62)	—	170

$Rh_2(OAc)_4$, CH_2Cl_2, 20°



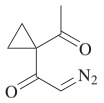
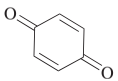
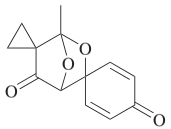
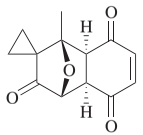
(16) 147

$Rh_2(OAc)_4$, CH_2Cl_2, rt



(68) 295

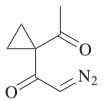
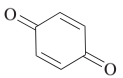
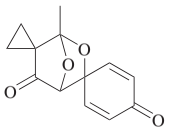
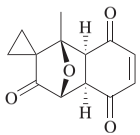
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		Catalyst, rt	 **I** +  **II**	166

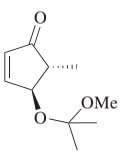
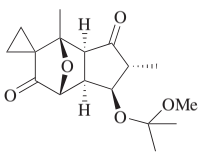
Catalyst	Solvent	I + II	I/II
$Rh_2(OAc)_4$	CH_2Cl_2	(41)	37:63
$Rh_2(OCHO)_4$	C_6H_6	(79)	58:42
$Pd[P(2\text{-}Tol)_3]_3Cl_2$	C_6H_6	(42)	57:43
$Rh_2(tpa)_4$	C_6H_6	(65)	55:45
$Rh_2(tfb)_4$	C_6H_6	(63)	52:48
$Rh_2(OAc)_4$	C_6H_6	(73)	52:48
$Rh_2(OCOC_6H_4Me)_4$	C_6H_6	(89)	52:48
$Rh_2(oct)_4$	C_6H_6	(66)	52:48
$Rh_2(OCOPh)_4$	C_6H_6	(90)	50:50
$Rh_2(OCOC_6H_4NMe_2)_4$	C_6H_6	(76)	50:50
$Rh_2(adc)_4$	C_6H_6	(88)	50:50
$Rh_2(tfa)_4$	C_6H_6	(87)	50:50
$Rh_2(OCOCH_2Cl)_4$	C_6H_6	(89)	47:53
$Rh_2(OCOC_6H_4F)_4$	C_6H_6	(80)	46:54
$Rh_2(Opiv)_4$	C_6H_6	(87)	46:54
$Pd(PPh_3)_3Cl_2$	C_6H_6	(57)	46:54
$Rh_2(OCOC_6H_4CO_2Me)_4$	C_6H_6	(93)	45:55
$Rh_2(OCOC_6H_4Cl)_4$	C_6H_6	(89)	45:55
$Rh_2(OCOC_6H_4CF_3)_4$	C_6H_6	(94)	45:55
$Rh_2(cap)_4$	C_6H_6	(65)	45:55

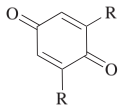
$Rh_2(OCOC_6H_4OMe)_4$	C_6H_6	(66)	43:57
$Rh_2(OCOC_6H_4Cl\text{-}3)_4$	C_6H_6	(99)	40:60
$Rh_2(OCOC_6H_4NO_2)_4$	C_6H_6	(81)	38:62
$Cu(acac)_2$	C_6H_6	(62)	35:65
$Rh_2(oct)_4$	CH_3NO_2	(69)	77:23
$Rh_2(oct)_4$	pentane	(79)	71:29
$Rh_2(oct)_4$	hexane	(78)	70:30
$Rh_2(oct)_4$	cyclohexane	(74)	68:32
$Rh_2(oct)_4$	C_6F_6	(82)	66:34
$Rh_2(oct)_4$	CCl_2FCF_2Cl	(91)	65:35
$Rh_2(oct)_4$	*t*-BuOMe	(71)	63:37
$Rh_2(oct)_4$	CCl_4	(85)	61:39
$Rh_2(oct)_4$	CS_2	(71)	61:39
$Rh_2(oct)_4$	Et_2O	(71)	61:39
$Rh_2(oct)_4$	CCl_4	(81)	61:39
$Rh_2(oct)_4$	DMF	(47)	60:40
$Rh_2(oct)_4$	C_6H_5Cl	(97)	57:43
$Rh_2(oct)_4$	$CHCl_3$	(75)	56:44
$Rh_2(oct)_4$	$CHClCCl_2$	(75)	56:44
$Rh_2(oct)_4$	1,4-$Me_2C_6H_4$	(78)	55:45

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

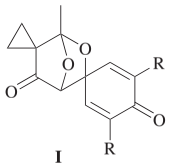
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
 (*Continued*)		Catalyst, rt	 **I** +  **II**	166

Catalyst	Solvent		er
$Rh_2(oct)_4$	CH_2Cl_2	(83)	54:46
$Rh_2(oct)_4$	DME	(76)	54:46
$Rh_2(oct)_4$	EtOAc	(65)	54:46
$Rh_2(oct)_4$	THF	(62)	53:47
$Rh_2(oct)_4$	$1,3\text{-}Me_2C_6H_4$	(76)	53:47
$Rh_2(oct)_4$	DCE	(84)	52:48
$Rh_2(oct)_4$	C_6H_6	(66)	52:48
$Rh_2(oct)_4$	MEK	(72)	50:50
$Rh_2(oct)_4$	C_6H_5F	(88)	49:51
$Rh_2(oct)_4$	$1,2\text{-}Me_2C_6H_4$	(92)	48:52
$Rh_2(oct)_4$	1,4-dioxane	(85)	46:54
$Rh_2(oct)_4$	toluene	(62)	45:55
$Rh_2(oct)_4$	CH_3CN	(65)	41:59
$Rh_2(OCOC_6H_4\text{-}3\text{-}Cl)_4$	$1,2\text{-}Me_2C_6H_4$	(74)	40:60

	$Rh_2(OAc)_4$, CH_2Cl_2, DMF, reflux		(84)	174

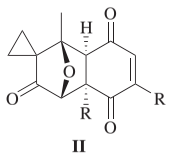


$Rh_2(OCOC_6H_4\text{-}3\text{-}Cl)_4$, 1,2-$Me_2C_6H_4$, rt



I

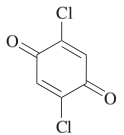
+



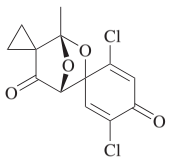
II

R	I + II	I/II
MeO	(66)	100:0
Me	(65)	27:73

166

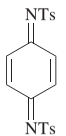


$Rh_2(OCOC_6H_4\text{-}3\text{-}Cl)_4$, 1,2-$Me_2C_6H_4$, rt

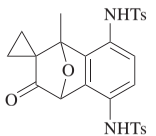


(64)

166



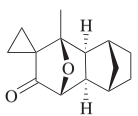
$Rh_2(OAc)_4$, C_6H_6, rt



(54)

296

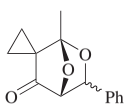
$Rh_2(OAc)_4$, C_6H_6, rt



(68)

58

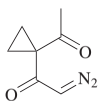
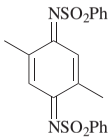
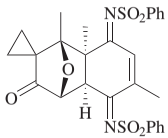
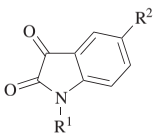
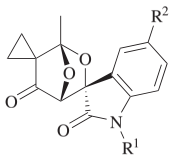
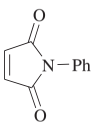
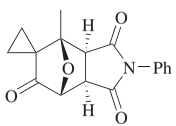
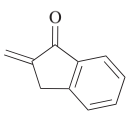
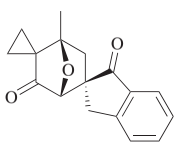
$Rh_2(OAc)_4$, $CHCl_3$, rt



(100) *exo*/*endo* = 4:1

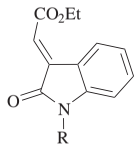
112

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

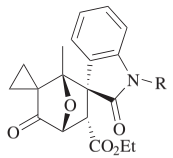
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$Rh_2(OAc)_4$, C_6H_6, rt	 (75)	296
		$Rh_2(OAc)_4$, toluene, rt		297
		$Rh_2(OAc)_4$, rt		112, 113
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (90)	169

R^1	R^2	
H	H	(52)
H	Br	(86)
Me	H	(82)
Et	H	(78)
Ph	H	(77)
Bn	H	(80)

Solvent		
$CHCl_3$	(79)	112, 113
$[bmim]BF_4$	(95)	190

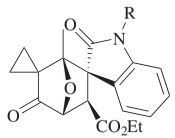


$Rh_2(OAc)_4$, toluene, rt



I

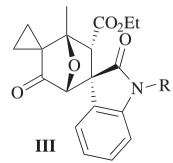
+



II

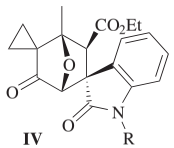
298

+



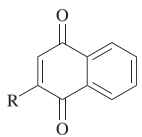
III

+

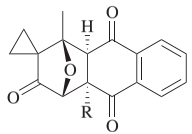


IV

R	I + II + III + IV	I/II/III/IV
H	(93)	1:1:1.5:1
Me	(93)	3:2:3:2
Bn	(98)	1:1:1:0

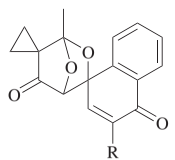


$Rh_2(OCOC_6H_4\text{-}3\text{-}Cl)_4$,
$1,2\text{-}Me_2C_6H_4$, rt



I

+

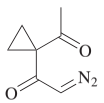
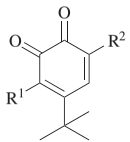
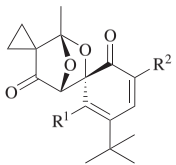
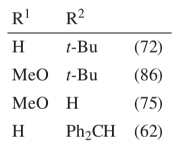
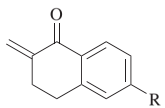
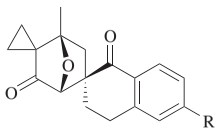
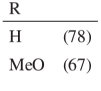
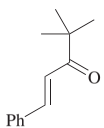
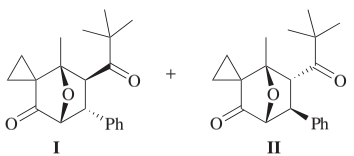
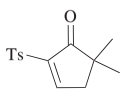
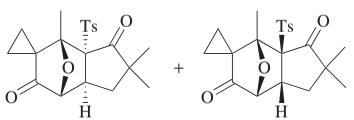


II

166

R	I + II	I/II
H	(61)	100:0
Me	(81)	91:9

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$Rh_2(OAc)_4$, toluene, rt	 	299
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 	169
		$Rh_2(oct)_4$, Et_2O, rt	 **I** **II** **I + II** (69), **I/II** = 2.5:1	170
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** **II** **I + II** (98), **I/II** = 2:1	300

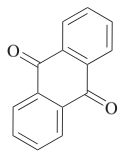
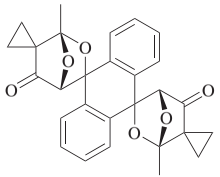
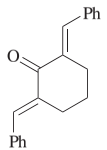
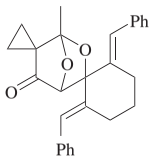
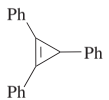
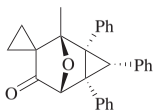
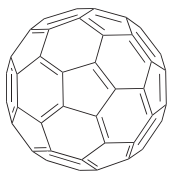
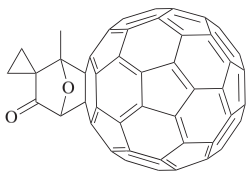
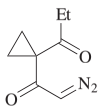
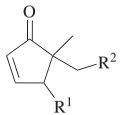
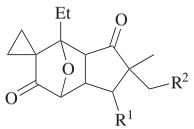
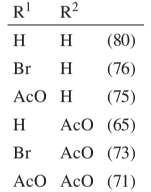
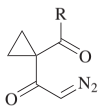
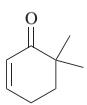
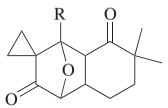
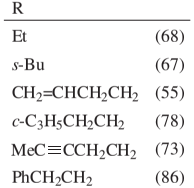
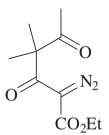
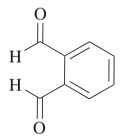
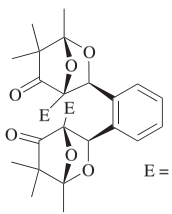
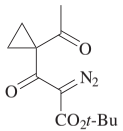
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(75)	188, 193
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(73)	180
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(72)	148
	$Rh_2(OAc)_4$, toluene, rt		(54)	146

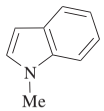
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		$Rh_2(oct)_4$, Et_2O, rt	 	170
C_{8-14} 		$Rh_2(oct)_4$, Et_2O, rt	 	170
C_8 		$Rh_2(OAc)_4$, C_6H_6, 80°	 (76) 	193

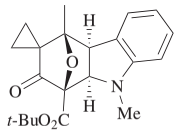
R	
Et	(68)
s-Bu	(67)
CH_2=$CHCH_2CH_2$	(55)
c-$C_3H_5CH_2CH_2$	(78)
MeC≡CCH_2CH_2	(73)
$PhCH_2CH_2$	(86)

R^1	R^2	
H	H	(80)
Br	H	(76)
AcO	H	(75)
H	AcO	(65)
Br	AcO	(73)
AcO	AcO	(71)



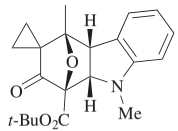


Catalyst **8f**, $PhCF_3$



I

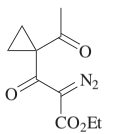
+



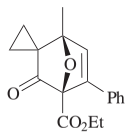
II

Temp (°)	**I** + **II**	**I**/**II**	er **I**	er **II**
23	(69)[e]	87:13	91.0:9.0	51.0:49.0
60	(88)	92:8	96.0:4.0	51.0:49.0

346



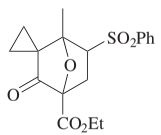
Catalyst **8f**, $PhCF_3$, 60°



(51) er 55.0:45.0

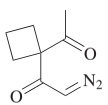
346

$Rh_2(OAc)_4$, C_6H_6, rt

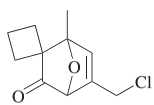


(68)

156



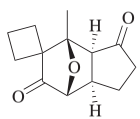
$Rh_2(OAc)_4$, 4 Å MS, C_6H_5Cl, rt



(65)

301

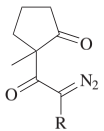
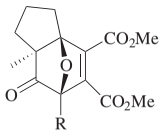
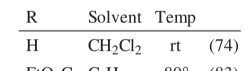
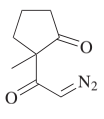
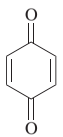
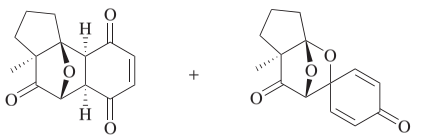
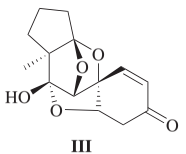
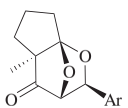
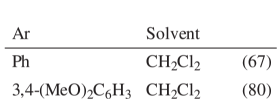
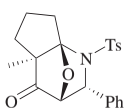
$Rh_2(OAc)_4$, C_6H_5Cl, rt



(37)

301

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9} 		$Rh_2(OAc)_4$	 	163
C_8 		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 	302
		$Rh_2(OAc)_4$, rt	 	176, 190, 190
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (54)	196, 303

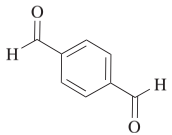
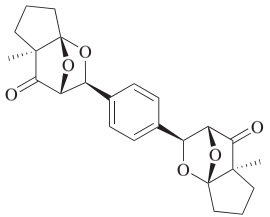
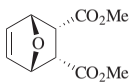
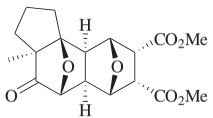
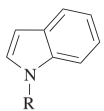
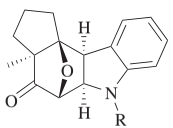
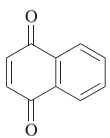
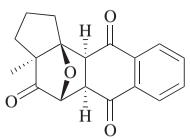
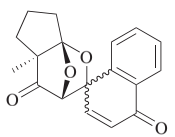
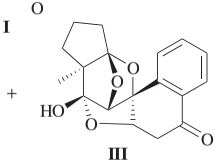
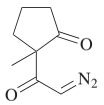
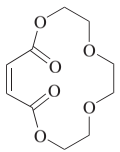
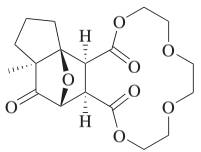
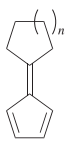
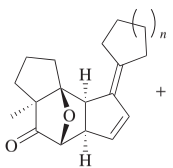
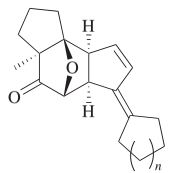
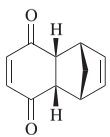
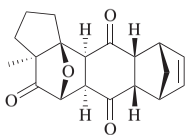
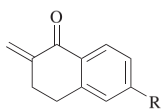
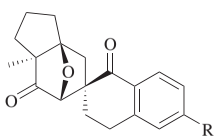
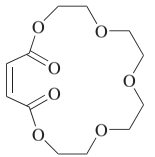
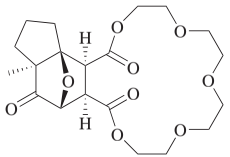
	$Rh_2(OAc)_4$, C_6H_6, 80°		(55)	193
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(79)	293
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		R H (34) Me (44)	160, 161
	$Rh_2(OAc)_4$, C_6H_6, rt	 **I** +  **II** +  **III**	**I** + **II** + **III** (37) **I**/**II**/**III** = 24:8:5	302

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

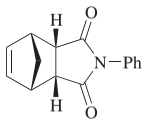
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (64)	294
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** +  **II**	304
			n **I** **II** 1 (58) (5) 2 (66) (6)	
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (81)	293
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		169
			R (60) H MeO (51)	



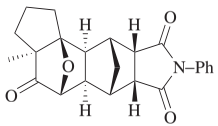
$Rh_2(OAc)_4$, CH_2Cl_2, rt



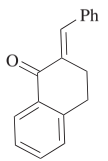
(68) 294



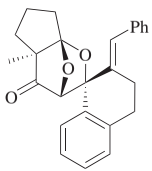
$Rh_2(OAc)_4$, CH_2Cl_2, rt



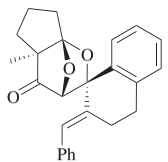
(78) 293



$Rh_2(OAc)_4$, CH_2Cl_2, rt

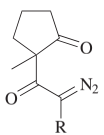


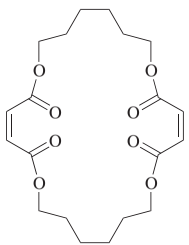
(26) +



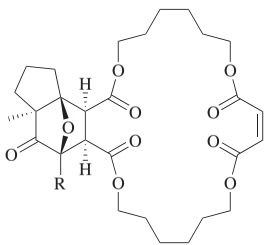
(17) 180, 181

C_{8-9}





$Rh_2(OAc)_4$, CH_2Cl_2

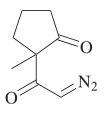
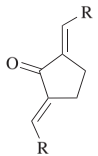
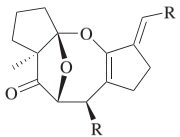
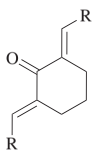
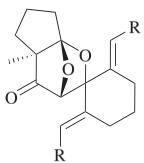
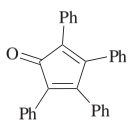
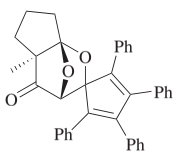
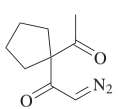
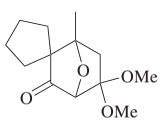


(60)

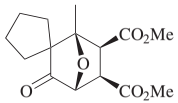
R	Temp
H	rt
EtO_2C	reflux

294

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

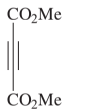
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		1. $Rh_2(OAc)_4$, CH_2Cl_2, rt 2. Al_2O_3 chromatography	 R: PhCH=CH (31); 2-$MeOC_6H_4CH$=CH (34)	180
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (74) R: Ph; (*E*)-PhCH=CH	178 178, 180
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (60)	176
C_9				
		$Rh_2(OAc)_4$, rt	 (60)	58

$Rh_2(OAc)_4$, CH_2Cl_2, rt

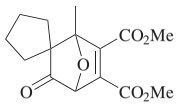


(36)

58



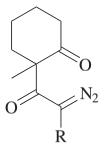
$Rh_2(OAc)_4$, CH_2Cl_2, rt



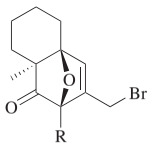
(80)

58

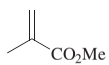
C_{9-10}



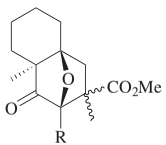
$Rh_2(OAc)_4$



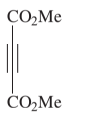
R	Solvent	Temp		
H	CH_2Cl_2	rt	(56)	163
H	[bmim]BF_4	rt	(68)	190
EtO_2C	C_6H_6	80°	(63)	163



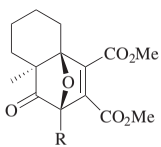
$Rh_2(OAc)_4$



R	Solvent	Temp		dr	
H	CH_2Cl_2	rt	(63)	5:1	163
EtO_2C	C_6H_6	80°	(86)	2:1	

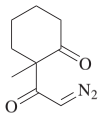
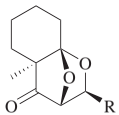
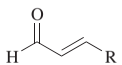
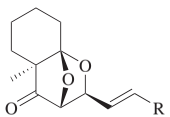
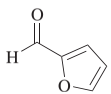
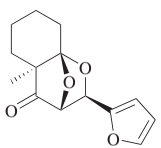
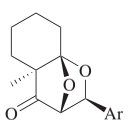


$Rh_2(OAc)_4$



R	Solvent	Temp		
H	CH_2Cl_2	rt	(76)	163
H	[bmim]BF_4	rt	(87)	190
EtO_2C	C_6H_6	80°	(88)	163

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Rh_2(OAc)_4$, rt		176, 190
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		176
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		176
		$Rh_2(OAc)_4$, rt		190

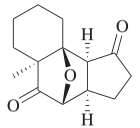
R	Solvent		
4-$MeOC_6H_4$	CH_2Cl_2	(73)	176
3,4-$(MeO)_2C_6H_3$	CH_2Cl_2	(81)	190
3,4-$(MeO)_2C_6H_3$	$[bmim]BF_4$	(89)	190
4-MeC_6H_4	CH_2Cl_2	(79)	176
4-MeC_6H_4	$[bmim]BF_4$	(85)	190

R		
Me	(67)	176
Ph	(86)	

(68) 176

Ar	Solvent		
9-anthryl	CH_2Cl_2	(84)	190
9-anthryl	$[bmim]BF_4$	(86)	
1-pyrenyl	$[bmim]BF_4$	(95)	

$Rh_2(OAc)_4$, CH_2Cl_2, rt



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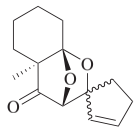
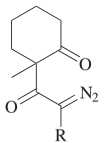


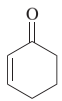
176

I **II**

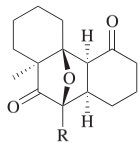
I + **II** (50), **I**/**II** = 44:6, **II** dr 3:1

C_{9-10}





$Rh_2(OAc)_4$



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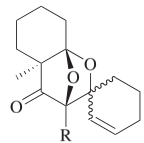
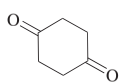


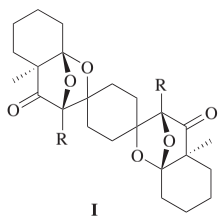
176

I **II**

R	Solvent	Temp	**I**	**II**	dr **II**
H	CH_2Cl_2	rt	(64)	(23)	3:1
EtO_2C	C_6H_6	80°	(12)	(67)	3:1



$Rh_2(OAc)_4$



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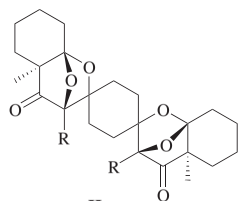
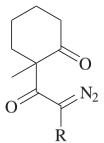
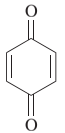
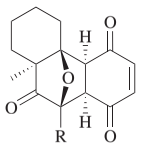
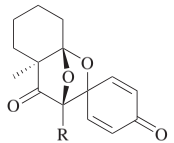
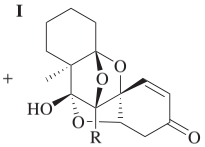


188

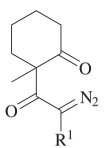
I **II**

R	Solvent	Temp	**I**	**II**
H	CH_2Cl_2	rt	(45)	(17)
EtO_2C	C_6H_6	80°	(75)	(0)

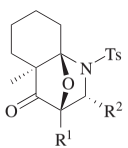
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 		$Rh_2(OAc)_4$, C_6H_6	 +  **I** **II** +  **III**	302

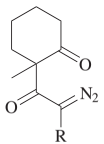
R	Temp	I	II	III
H	rt	(6)	(18)	(35)
EtO_2C	80°	(4)	(17)	(27)

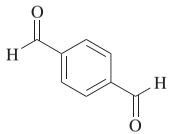


$Rh_2(OAc)_4$

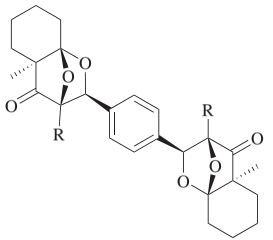


R^1	R^2	Solvent	Temp		Refs.
H	Ph	CH_2Cl_2	rt	(71)	196, 303
H	3-FC_6H_4	CH_2Cl_2	rt	(70)	196, 303
H	2-BrC_6H_4	CH_2Cl_2	rt	(62)	196
H	2-ClC_6H_4	CH_2Cl_2	rt	(77)	303
H	4-FC_6H_4	CH_2Cl_2	rt	(77)	303
H	4-MeC_6H_4	CH_2Cl_2	rt	(56)	196
EtO_2C	Ph	C_6H_6	80°	(60)	196





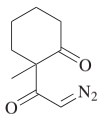
$Rh_2(OAc)_4$, C_6H_6, 80°

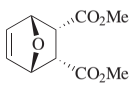


R	
H	(63)
EtO_2C	(58)

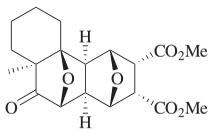
193

C_9



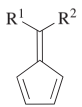


$Rh_2(OAc)_4$, CH_2Cl_2, rt

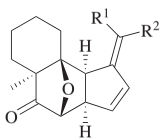


(82)

293



$Rh_2(OAc)_4$, CH_2Cl_2, rt



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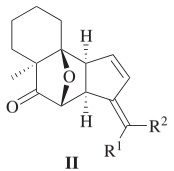

I **II**

R^1	R^2	**I**	**II**
H	4-ClC_6H_4	(58)	(31)
H	4-$Me_2NC_6H_4$	(56)	(30)
H	4-$MeOC_6H_4$	(46)	(25)
H	4-MeC_6H_4	(53)	(27)
Me	Me	(57)	(7)

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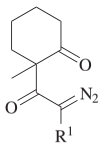
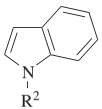
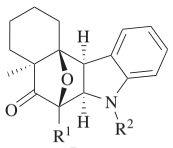
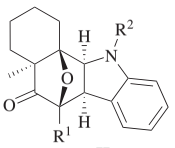
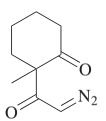
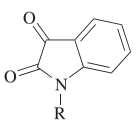
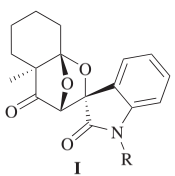
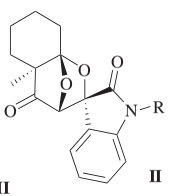
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

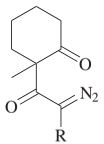
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 		$Rh_2(OAc)_4$	 +  **I** **II**	160, 161

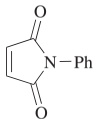
R^1	R^2	Solvent	Temp	**I**	**II**
H	H	CH_2Cl_2	rt	(71)	(0)
H	Me	CH_2Cl_2	rt	(84)	(0)
H	Bn	CH_2Cl_2	rt	(85)	(0)
H	PhCO	CH_2Cl_2	rt	(22)	(14)
H	PhO_2S	CH_2Cl_2	rt	(8)	(24)
EtO_2C	H	C_6H_6	reflux	(69)	(0)
EtO_2C	Me	C_6H_6	reflux	(82)	(0)
EtO_2C	Bn	C_6H_6	reflux	(86)	(0)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 +  **I** **II**	293

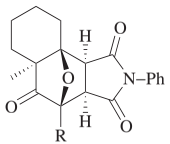
R	**I**	**II**
H	(46)	(30)
Me	(53)	(34)

C_{9-10}



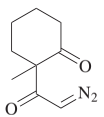


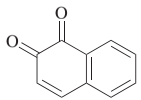
$Rh_2(OAc)_4$



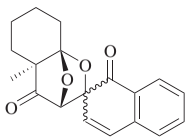
R	Solvent	Temp		
H	CH_2Cl_2	rt	(88)	163
H	$[bmim]BF_4$	rt	(91)	190
EtO_2C	C_6H_6	80°	(95)	163

C_9



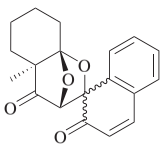


$Rh_2(OAc)_4$, CH_2Cl_2, rt



(38) dr 3.75:1

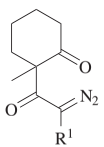
+

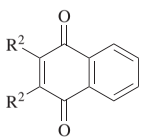


(19) dr 3.4:1

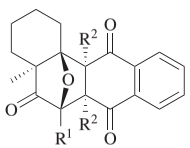
179

C_{9-10}



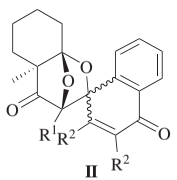


$Rh_2(OAc)_4$, C_6H_6



I

+

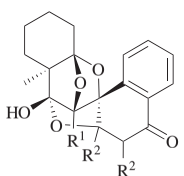


II

302

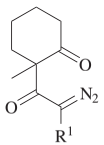
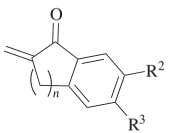
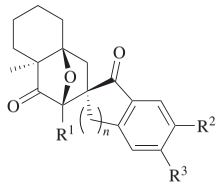
R^1	R^2	Temp	**I + II + III**	**I/II/III**
H	H	rt	(54)	33:14:7
H	Cl	rt	(34)	4:30:0
EtO_2C	H	80°	(38)	25:5:8

+

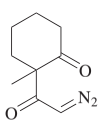
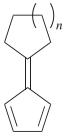


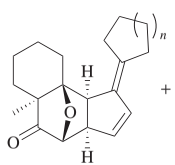
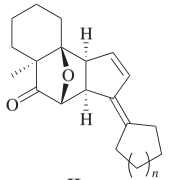
III

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 		$Rh_2(OAc)_4$		169

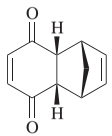
n	R^1	R^2	R^3	Solvent	Temp	
1	H	H	H	CH_2Cl_2	rt	(94)
1	H	MeOCHN	H	CH_2Cl_2	rt	(66)
2	H	H	H	CH_2Cl_2	rt	(89)
2	H	H	MeO	CH_2Cl_2	rt	(95)
2	H	Br	H	CH_2Cl_2	rt	(63)
2	H	MeOCHN	H	CH_2Cl_2	rt	(64)
2	EtO_2C	H	H	C_6H_6	80°	(93)
2	EtO_2C	H	MeO	C_6H_6	80°	(90)

C_9  

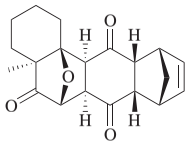
$Rh_2(OAc)_4$, CH_2Cl_2, rt  + 

I **II**

n	**I**	**II**	
1	(62)	(6)	304
2	(57)	(6)	
3	(60)	(5)	

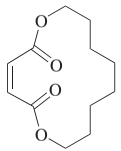


$Rh_2(OAc)_4$, CH_2Cl_2, rt

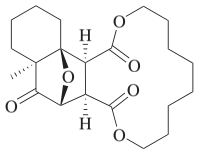


(85)

293



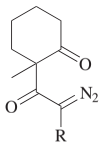
$Rh_2(OAc)_4$, CH_2Cl_2, rt

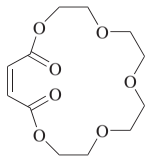


(74)

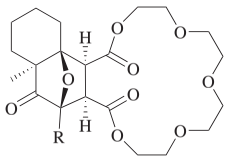
294

C_{9-10}



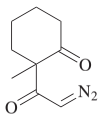


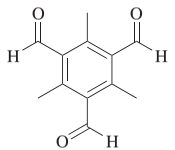
$Rh_2(OAc)_4$



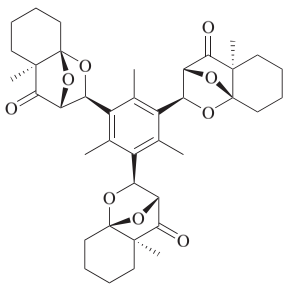
R	Solvent	Temp		
H	CH_2Cl_2	rt	(72)	294
EtO_2C	C_6H_6	80°	(70)	

C_9





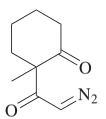
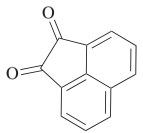
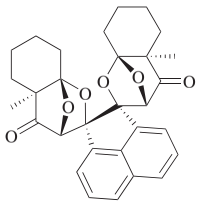
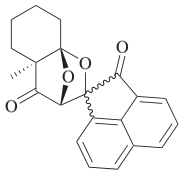
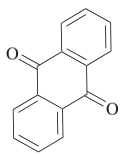
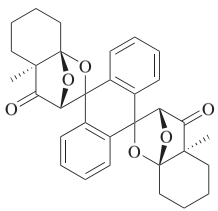
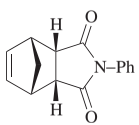
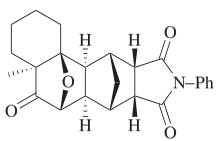
$Rh_2(OAc)_4$, CH_2Cl_2, rt



(65)

193

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** (20) +  **II** (31) + **III** (19)	188
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (60)	188, 193
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (81)	293

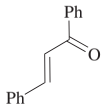
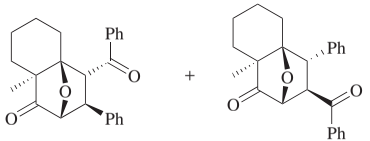
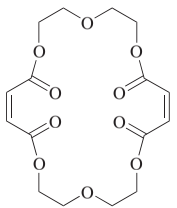
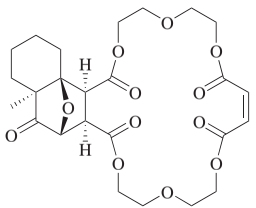
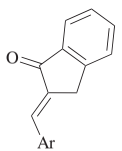
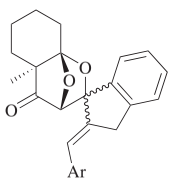
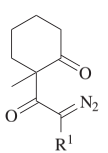
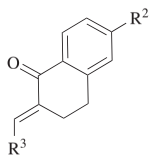
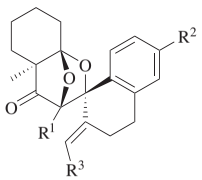
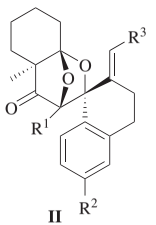
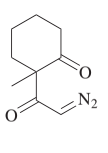
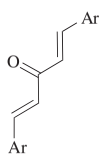
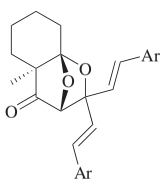
	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** + **II** (57), **I/II** = 2.1:1		176
	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(60)	294
 Ar = 4-ClC_6H_4	$Rh_2(OAc)_4$, CH_2Cl_2, rt		(49) dr 2:3	180

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

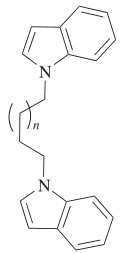
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10} 		$Rh_2(OAc)_4$	 +  **I** **II**	

R^1	R^2	R^3	Solvent	Temp	**I**	**II**	**I + II**	dr	Refs.
H	H	Ph	CH_2Cl_2	rt	(21)	(33)	(—)	—	180, 181
H	H	4-FC_6H_4	CH_2Cl_2	rt	(—)	(—)	(47)	3:2	181
H	H	4-ClC_6H_4	CH_2Cl_2	rt	(—)	(—)	(44)	3:2	181
H	H	4-$MeOC_6H_4$	CH_2Cl_2	rt	(—)	(—)	(48)	3:2	181
H	H	4-MeC_6H_4	CH_2Cl_2	rt	(—)	(—)	(49)	3:2	181
H	MeO	4-$MeOC_6H_4$	CH_2Cl_2	rt	(41)	(20)	(—)	—	180
H	MeO	4-ClC_6H_4	CH_2Cl_2	rt	(40)	(20)	(—)	—	180
EtO_2C	H	Ph	C_6H_6	80°	(—)	(—)	(49)	3:2	181

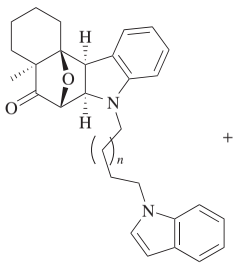
C_9  

$Rh_2(OAc)_4$, CH_2Cl_2, rt 

Ar		Refs.
4-$MeOC_6H_4$	(74)	178
4-MeC_6H_4	(73)	



$Rh_2(OAc)_4$, CH_2Cl_2, rt



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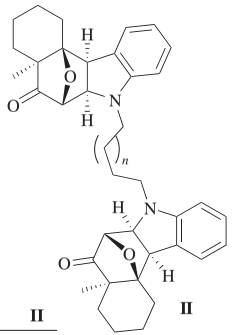


161

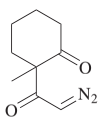
I

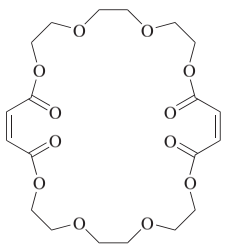
n	**I**	**II**
0	(23)	(65)
1	(29)	(57)

II

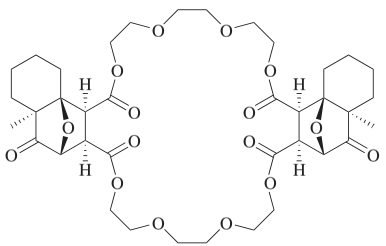
283

C_9





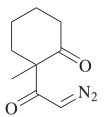
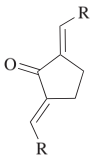
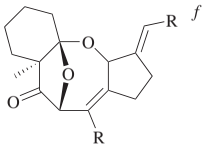
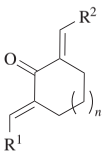
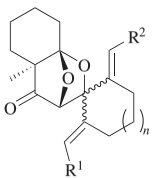
$Rh_2(OAc)_4$, CH_2Cl_2, rt



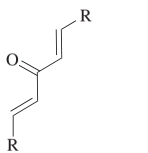
(48)

294

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

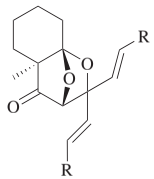
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. $Rh_2(OAc)_4$, CH_2Cl_2, rt 2. Al_2O_3 chromatography	 *f* R (*E*)-PhCH=CH (28) (*E*)-4-$MeOC_6H_4$CH=CH (32)	180
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		

n	R^1	R^2		dr	
0	2-furyl	2-furyl	(70)	—	178, 180
0	4-ClC_6H_4	4-ClC_6H_4	(71)	—	178
0	(*E*)-PhCH=C(Me)	(*E*)-PhCH=C(Me)	(73)	—	180
0	1-naphthyl	1-naphthyl	(74)	—	180
1	Ph	Ph	(79)	—	178
1	Ph	4-MeC_6H_4	(90)	2:1	180
1	4-ClC_6H_4	4-ClC_6H_4	(70)	—	178, 180
1	4-$MeOC_6H_4$	4-$MeOC_6H_4$	(78)	—	178
1	2,4-$(MeO)_2C_6H_3$	2,4-$(MeO)_2C_6H_3$	(76)	—	178
1	1-naphthyl	1-naphthyl	(76)	—	178
1	(*E*)-PhCH=CH	(*E*)-PhCH=CH	(74)	—	178, 180
2	4-ClC_6H_4	4-ClC_6H_4	(55)	—	178

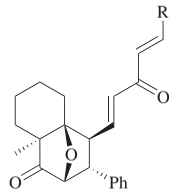


R = (*E*)-PhCH=CH

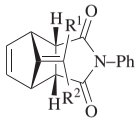
$Rh_2(OAc)_4$, CH_2Cl_2, rt



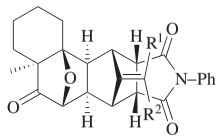
(41) + (25)



180



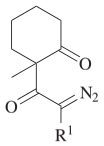
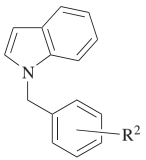
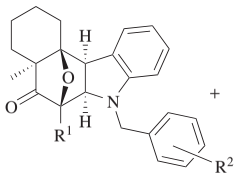
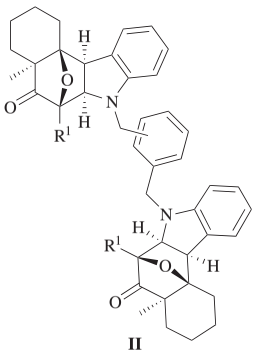
$Rh_2(OAc)_4$, CH_2Cl_2, rt



293

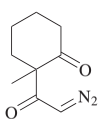
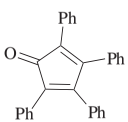
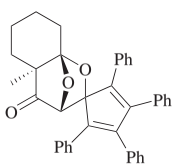
R^1	R^2	Time (h)	
H	4-MeC_6H_4	4	(79)
H	4-MeC_6H_4	3.5	(82)
H	4-ClC_6H_4	4	(79)
—$(CH_2)_4$—		3.5	(84)

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

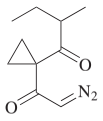
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10}				
		$Rh_2(OAc)_4$	 + 	161

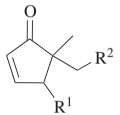
I **II**

R^1	R^2	Solvent	Temp	**I**	**II**
H	2-indol-1-ylmethyl	CH_2Cl_2	rt	(40)	(52)
H	2-indol-1-ylmethyl	DCE	rt	(39)	(48)
H	3-indol-1-ylmethyl	CH_2Cl_2	rt	(36)	(63)
H	4-indol-1-ylmethyl	CH_2Cl_2	rt	(45)	(50)
EtO_2C	2-indol-1-ylmethyl	C_6H_6	reflux	(27)	(69)
EtO_2C	2-indol-1-ylmethyl	DCE	reflux	(—)	(85)
EtO_2C	3-indol-1-ylmethyl	C_6H_6	reflux	(24)	(70)
EtO_2C	3-indol-1-ylmethyl	DCE	reflux	(—)	(89)
EtO_2C	4-indol-1-ylmethyl	C_6H_6	reflux	(9)	(80)
EtO_2C	4-indol-1-ylmethyl	DCE	reflux	(—)	(84)

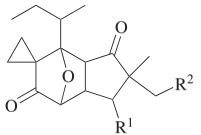
C_9				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (65)	176

C_{10}



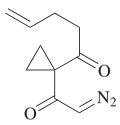


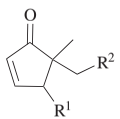
$Rh_2(oct)_4$, Et_2O, rt



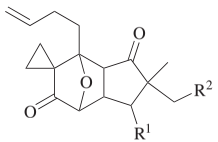
R^1	R^2	
H	H	(85)
Br	H	(76)
AcO	H	(86)
H	AcO	(84)
Br	AcO	(78)
AcO	AcO	(76)

170





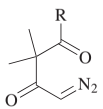
$Rh_2(oct)_4$, Et_2O, rt



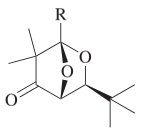
R^1	R^2	
H	H	(79)
Br	H	(91)
AcO	H	(84)
H	AcO	(59)
Br	AcO	(67)
AcO	AcO	(46)

170

C_{10-12}



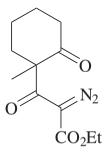
$Rh_2(OAc)_4$, CH_2Cl_2, rt

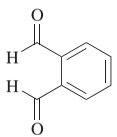


R	
TBDPSO$(CH_2)_4$	(80)
n-C_6H_{13}	(89)

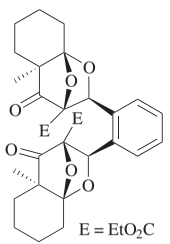
194

C_{10}





$Rh_2(OAc)_4$, C_6H_6, 80°

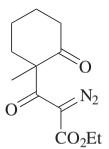
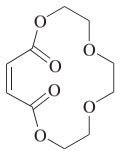
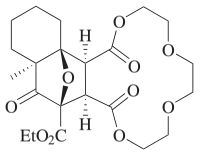
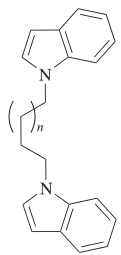
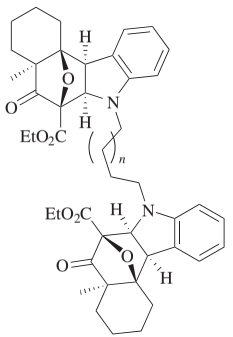
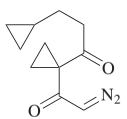
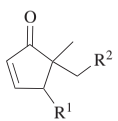
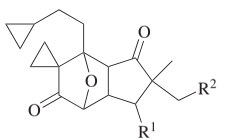


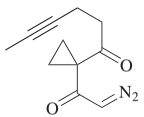
E = EtO_2C

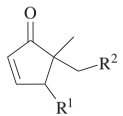
(65)

193

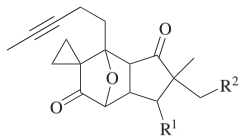
TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		$Rh_2(OAc)_4$, C_6H_6, reflux	 (76)	294
		$Rh_2(OAc)_4$, DCE, rt	 *n*: 0 (85); 1 (80)	161
C_{11}				
		$Rh_2(oct)_4$, Et_2O, rt	 R^1 R^2: H H (82); Br H (80); AcO H (50); H AcO (73); Br AcO (73); AcO AcO (66)	170



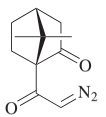


$Rh_2(oct)_4$, Et_2O, rt

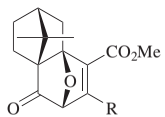


R^1	R^2	
H	H	(85)
Br	H	(100)
AcO	H	(89)
H	AcO	(88)
Br	AcO	(86)
AcO	AcO	(73)

170

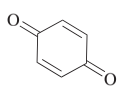


$Rh_2(OAc)_4$, C_6H_6, rt

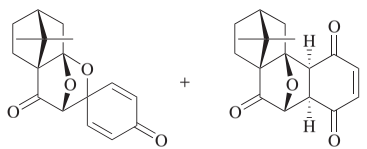


R	
H	(72)
MeO_2C	(85)

112, 113



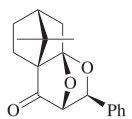
$Rh_2(OCOC_6H_4\text{-}3\text{-}Cl)_4$, $1,2\text{-}Me_2C_6H_4$, rt



I + **II** (58), **I**/**II** = 76:24

166

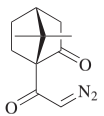
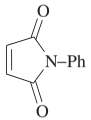
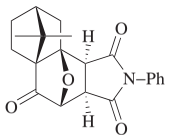
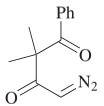
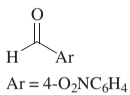
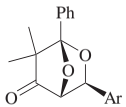
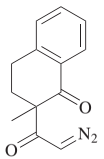
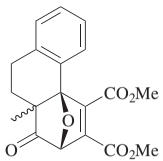
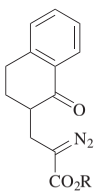
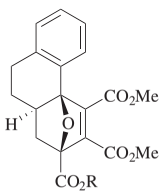
$Rh_2(OAc)_4$, C_6H_6, rt



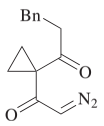
(66)

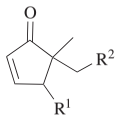
112, 113

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

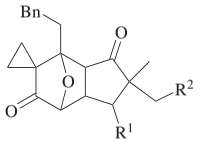
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		$Rh_2(OAc)_4$, C_6H_6, rt	 (62)	112
C_{12} 	 Ar = 4-$O_2NC_6H_4$	Catalyst **9c**, $PhCF_3$, 0°	 (62) er <50.5:49.5	99
C_{13} 		$Rh_2(OAc)_4$, rt	 dr 3:1	Solvent: CH_2Cl_2 (85); $[bmim]BF_4$ (88) — 190
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		R: Et (92) — 120; $CH_2=CHCH_2$ (89) — 43, 120; $CH_2=CHCH_2CH_2$ (90) — 43

C_{14}



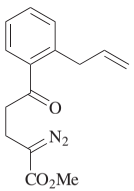


$Rh_2(oct)_4$, Et_2O, rt

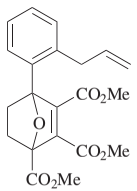


R^1	R^2	
H	H	(87)
Br	H	(100)
AcO	H	(81)
H	AcO	(93)
Br	AcO	(100)
AcO	AcO	(83)

170



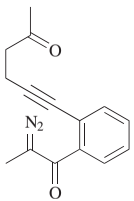
$Rh_2(OAc)_4$, CH_2Cl_2, rt



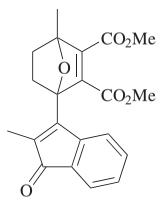
(85)

43, 120

C_{15}



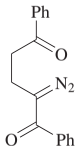
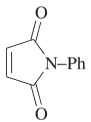
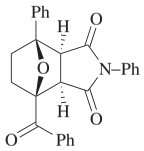
Catalyst, CH_2Cl_2, rt



(97)

Catalyst	
$Rh_2(oct)_4$	108
$Rh_2(OAc)_4$	107

TABLE 9. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (89)	120

[a]The yield was determined by NMR analysis. The yield of isolated product was 73%.

[b]The ionic liquid was recycled.

[c]After the addition of the diazo compound and the dipolarophile over 1 h, the reaction mixture was stirred for an additional 23 h.

[d]The product was a mixture of isomers.

[e]After the addition of the diazo compound and the dipolarophile over 1 h, the reaction mixture was stirred for an additional 7 h.

[f]The product results from ring expansion of the intermediate cycloadduct.

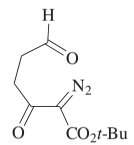
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES

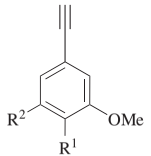
A. NON-AROMATIC YLIDES

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.

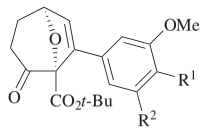
See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*

C_6

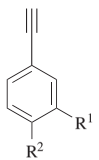




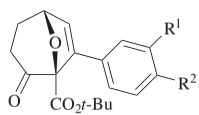
Catalyst *ent*-**8f**, $PhCF_3$, rt



R^1	R^2		er	
HO	H	(77)	97.5:2.5	
HO	MeO	(55)	75.0:25.0	306
TBSO	MeO	(39)	63.0:37.0	
MeO	MeO	(44)	60.0:40.0	
AcO	MeO	(62)	50.5:49.5	

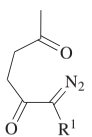


Catalyst **8f**, $PhCF_3$, rt

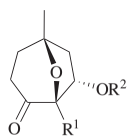


R^1	R^2		er	
H	H	(75)	98.5:1.5	305
MeO	HO	(73)	97.5:2.5	305, 306
MeO	TBSO	(50)	67.5:32.5	305
MeO	AcO	(66)	90.5:9.5	305
MeO	BnO	(72)	94.0:6.0	305

C_{6-7}



$Rh_2(OAc)_4$, C_6H_6



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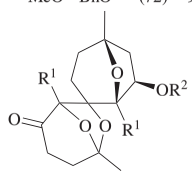
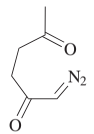
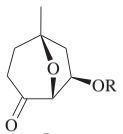
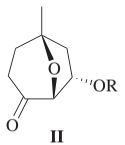


I **II**

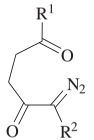
R^1	R^2	Temp (°)	**I**	**II**	
H	Ac	rt	(40)	(30)	45
H	Et	rt	(24)	(28)	45
H	TMS	70	(16)	(0)	151
H	Bn	70	(15)	(0)	151
EtO_2C	TMS	70	(66)	(0)	151
EtO_2C	TBS	70	(65)	(0)	151
EtO_2C	Bn	70	(48)	(0)	151

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

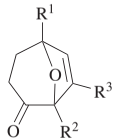
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		$Rh_2(OAc)_4$ (2 mol %), ligand/M(OTf)$_3$ (10 mol %), 4 Å MS	 **I** +  **II**	

R	Ligand	M	Solvent	Temp	I + II	I/II	er I	
Et	**16c**	Lu	CH_2Cl_2/MeOH (9:1)	rt	(52)	>99:1	—	104
n-Bu	**16a**	Eu	CH_2Cl_2	rt	(79)[a]	81:19	58.0:42.0	104
n-Bu	**16b**	Eu	CH_2Cl_2	rt	(68)[a]	84:16	71.5:28.5	104
n-Bu	**16c**	Eu	CH_2Cl_2	rt	(63)[a]	84:16	80.0:20.0	104
n-Bu	**16c**	Tm	CH_2Cl_2	rt	(68)[a]	88:12	83.5:16.5	103, 104
n-Bu	**16c**	Tm	CH_2Cl_2	30°	(60)[a]	91:9	87.5:12.5	104
n-Bu	**16c**	Tm	CH_2Cl_2	30°	(71)[b]	91:9	88.0:12.0	104
n-Bu	**16c**	Tm	CH_2Cl_2	30°	(70)[b,c]	90:10	82.5:17.5	104
n-Bu	**16c**	Tm	toluene	30°	(68)[b,d]	95:5	84.0:16.0	104
n-Bu	**16c**	Tm	CH_2Cl_2	35°	(55)[a]	90:10	84.0:16.0	104
n-Bu	**16c**	Tm	CH_2Cl_2	reflux	(65)[a]	86:14	76.5:23.5	104
n-Bu	**16c**	Lu	CH_2Cl_2	rt	(57)[a]	86:14	88.5:11.5	104
n-Bu	**16c**	Lu	CH_2Cl_2	rt	(68)[b]	89:11	89.0:11.0	104
n-Bu	**16c**	Lu	CH_2Cl_2	rt	(70)[b,c]	90:10	82.5:17.5	104
n-Bu	**16c**	Lu	CH_2Cl_2	rt	(64)[b,e]	92:8	91.0:9.0	104
n-Bu	**16c**	Lu	CH_2Cl_2	rt	(53)[b,e,f]	90:10	87.5:12.5	104
n-Bu	**16c**	Lu	CH_2Cl_2	rt	(62)[b,e,g]	94:16	82.0:18.0	104
n-Bu	**16c**	Lu	CH_2Cl_2	30°	(63)[b]	87:13	86.5:13.5	104
n-Bu	**16c**	Lu	CH_2Cl_2	35°	(64)[b]	89:11	86.0:14.0	104



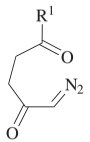
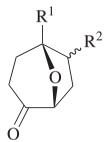
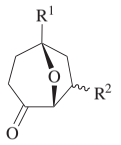
Catalyst



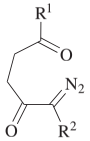
R^1	R^2	R^3	Catalyst	Solvent	Temp		er	
Me	H	EtO	$Rh_2(OAc)_4$	C_6H_6	70°	(17)	—	151
Me	H	$ClCH_2$	$Rh_2(OAc)_4$	C_6H_6	rt	(80)	—	45
Me	H	$MeOCH_2$	$Rh_2(OAc)_4$	C_6H_6	rt	(60) + 2:1 cycloadduct (26)	—	45
Me	MeO_2C	EtO	$Rh_2(OAc)_4$	C_6H_6	70°	(72)	—	151
Me	*t*-BuO_2C	EtO	**8f**	$PhCF_3$	rt	(93)	92.5:7.5	48
Ph	*t*-BuO_2C	EtO	**8f**	$PhCF_3$	rt	(85)	94.5:5.5	48
4-ClC_6H_4	*t*-BuO_2C	EtO	**8f**	$PhCF_3$	rt	(84)	94.0:6.0	48
4-$MeOC_6H_4$	*t*-BuO_2C	EtO	**8f**	$PhCF_3$	rt	(60)	97.0:3.0	48
4-MeC_6H_4	*t*-BuO_2C	EtO	**8f**	$PhCF_3$	rt	(75)	96.0:4.0	48

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

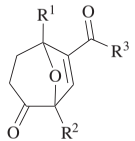
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-11} 		Catalyst, rt	 **I** +  **II**	

R^1	R^2	Catalyst	Solvent	**I** + **II**	**I**/**II**	*exo*/*endo* **I**	*exo*/*endo* **II**	
Me	MeO_2C	$Rh_2(OAc)_4$	CH_2Cl_2	(87)	2:1	3:1	3:1	171
Me	MeO_2C	$Rh_2(OAc)_4$	C_6H_6	(90)	1.7:1	2.8:1	1.8:1	45
Me	MeO_2C	**1a**	CH_2Cl_2	(85)	2.5:1	4:1	5:1	171
Me	MeO_2C	**1a**	C_6H_6	(73)	3:1	4:1	5:1	171
Me	MeO_2C	**1c**	CH_2Cl_2	(80)	2.6:1	3.8:1	7:1	171
Me	MeO_2C	**1b**	CH_2Cl_2	(82)	3:1	3.9:1	7:1	171
Me	MeO_2C	**1d**	CH_2Cl_2	(83)	4.8:1	3.8:1	3.3:1	171
Me	MeO_2C	**1e**	CH_2Cl_2	(78)	4.5:1	3.2:1	3.3:1	171
Me	MeOC	$Rh_2(OAc)_4$	C_6H_6	(90)	1:3.7	100:0	5.5:1	45
Ph	MeO_2C	$Rh_2(OAc)_4$	C_6H_6	(95)	75:20	9.7:1	2.3:1	45
Ph	MeO_2C	**1a**	CH_2Cl_2	(78)	5:1	15:1	5:1	171
Ph	MeO_2C	$Rh_2(OAc)_4$	C_6H_6	(90)	33:57	2.7:1	13:1	45
Ph	Ph	$Rh_2(OAc)_4$	C_6H_6	(90)	37:53	2.7:1	4.3:1	45

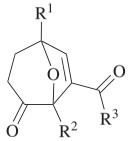


Catalyst



I

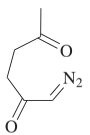
+



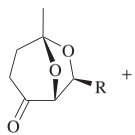
II

R^1	R^2	R^3	Catalyst	Solvent	Temp	**I + II**	**I/II**	
Me	H	MeO	$Rh_2(OAc)_4$	C_6H_6	rt	(78)	4:1	45, 290
Me	H	MeO	$Rh_2(OAc)_4$	C_6H_6	70°	(80)	—	151
Me	H	MeO	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(—)	8:1	171
Me	H	MeO	**1a**	CH_2Cl_2	rt	(80)	15:1	171
Me	H	Me	$Rh_2(OAc)_4$	C_6H_6	rt	(80)	4:1	45
Me	MeO_2C	MeO	$Rh_2(OAc)_4$	C_6H_6	70°	(16)	0:100	151
Ph	H	MeO	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(77)	100:0	171
Ph	H	MeO	**1a**	CH_2Cl_2	rt	(77)	100:0	171
Ph	H	MeO	$Rh_2(OAc)_4$	C_6H_6	rt	(89)	100:0	45
Ph	H	MeO	$Rh_2(OAc)_4$	C_6H_6	rt	(89)	13.8:1	290
Ph	H	Me	$Rh_2(OAc)_4$	C_6H_6	rt	(95)	100:0	45

C_6

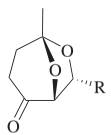


$Rh_2(OAc)_4$, C_6H_6, rt



I

+

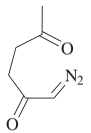
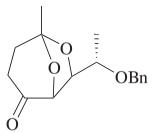
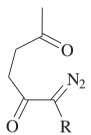
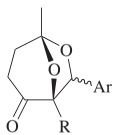
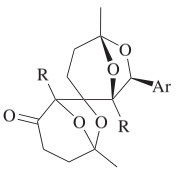


II

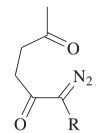
R	**I + II**	**I/II**	
Et	(60)	2:1	45, 191
n-$C_{10}H_{21}$	(75)	2:1	

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

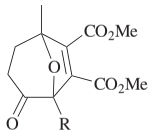
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		$Rh_2(OAc)_4$, C_6H_6, rt	 ("high") low dr	191
C_{6-7} 		Catalyst	 +  **I** **II**	

R	Ar	Catalyst	Solvent	Temp	**I**		er	**II**	
H	Ph	$Rh_2(OAc)_4$	C_6H_6	rt	(85)	*exo*	—	(7)	45, 290
H	Ph	**1a**	CH_2Cl_2	rt	(73)	*exo*	—	(—)	171
H	4-$O_2NC_6H_4$	**9c**	$PhCF_3$	0°	(14)	*exo*	59.5:40.5	(—)	99
MeO_2C	Ph	$Rh_2(OAc)_4$	C_6H_6	70°	(7)	—	—	(—)	151
MeO_2C	4-$MeOC_6H_4$	$Rh_2(OAc)_4$	C_6H_6	70°	(16)	—	—	(—)	151



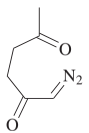
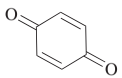
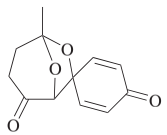
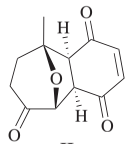
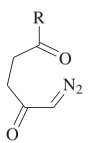
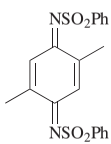
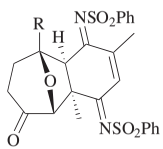
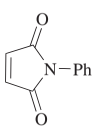
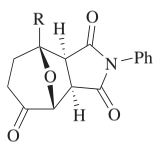
Catalyst



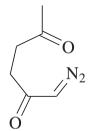
R	Catalyst	Solvent	Temp		er	
H	$Rh_2(OAc)_4$	C_6H_6	rt	(88)	—	45, 290
H	$Rh_2(OAc)_4$	[bmim]BF_4	rt	(84)	—	190
H	**1a**	CH_2Cl_2	rt	(83)	—	171
H	**2**, run 1	CH_2Cl_2	rt	(85)	—	171
H	**2**, run 2	CH_2Cl_2	rt	(83)	—	171
H	**2**, run 3	CH_2Cl_2	rt	(83)	—	171
H	**2**, run 4	CH_2Cl_2	rt	(81)	—	171
H	**2**, run 5	CH_2Cl_2	rt	(82)	—	171
H	**2**, run 6	CH_2Cl_2	rt	(80)	—	171
H	**2**, run 7	CH_2Cl_2	rt	(78)	—	171
H	**9c**	$PhCF_3$	rt	(50)	90.0:10.0	97
H	**9c**	$PhCF_3$	0°	(24)	91.0:9.0	97
EtO_2C	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(73)	—	120
EtO_2C	$Rh_2(OAc)_4$	toluene	85°	(91)	—	307
EtO_2C	**9c**	$PhCF_3$	rt	(23)	66.5:33.5	307
t-BuO_2C	**8f**	$PhCF_3$	rt	(60)	70.0:30.0	48
MeOC	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(89)	—	120
Me	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(75)	—	105
Me	**10b**	$PhCF_3$	20°	(61)	52.0:48.0	105
Me	**18**	$PhCF_3$	20°	(29)	58.5:41.5	105
Me	**8d**	$PhCF_3$	20°	(63)	61.0:39.0	105
Me	**9c**	$PhCF_3$	20°	(65)	75.5:24.5	105, 182

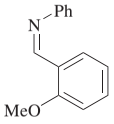
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

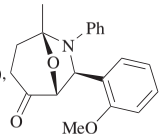
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		Catalyst, rt	 **I** +  **II**	
			Catalyst / Solvent / **I** / **II**: $Rh_2(OAc)_4$ / CH_2Cl_2 / (76) / (<10)	171
			1a / CH_2Cl_2 / (72) / (<10)	171
			$Rh_2(OCOC_6H_4\text{-}3\text{-}Cl)_4$ / 1,2-$Me_2C_6H_4$ / (48) / (—)	166
C_{6-11}				
		$Rh_2(OAc)_4$, C_6H_6, rt	 R: Me (61); Ph (66)	296
		Catalyst, rt	 R / Catalyst / Solvent: Me / $Rh_2(OAc)_4$ / C_6H_6 (87) 45; Me / $Rh_2(OAc)_4$ / CH_2Cl_2 (90) 171; Me / $Rh_2(OAc)_4$ / [bmim]BF_4 (90) 190; Me / **1a** / CH_2Cl_2 (82) 171; Ph / $Rh_2(OAc)_4$ / CH_2Cl_2 (88) 171; Ph / $Rh_2(OAc)_4$ / [bmim]BF_4 (86) 190; Ph / **1a** / CH_2Cl_2 (80) 171	

C_6



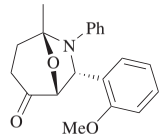


$Rh_2(OAc)_4$, CH_2Cl_2, rt,
$Rh_2(OAc)_4$, L.A. (10 mol %),
4 Å MS, CH_2Cl_2, rt



I

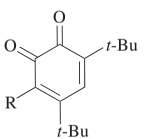
+



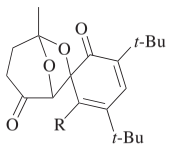
II

44

L.A.	**I + II**	**I/II**
—	(20)	54:46
$Yb(OTf)_3$	(74)	28:72

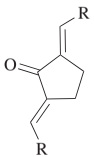


$Rh_2(OAc)_4$, toluene, rt

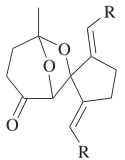


R	
H	(53)
MeO	(48)

299



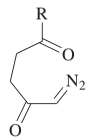
$Rh_2(OAc)_4$, CH_2Cl_2, rt

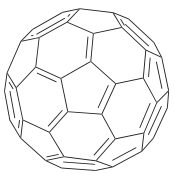


R	
(*E*)-$C_6H_5CH{=}CH$	(38)
2-$MeOC_6H_4CH{=}CH$	(47)

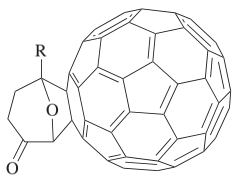
180

C_{6-12}





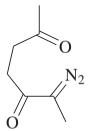
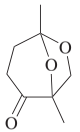
$Rh_2(OAc)_4$, toluene, rt



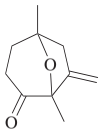
R		
Me	(40)	146
Ph	(45)	145, 146
4-ClC_6H_4	(39)	146
4-$MeOC_6H_4$	(31)	146
4-MeC_6H_4	(48)	145, 146

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

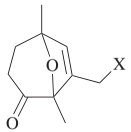
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		Catalyst, −78° to rt		105

Catalyst	Solvent		er
$Rh_2(OAc)_4$	CH_2Cl_2	(86)	—
10b	CH_2Cl_2	(26)	57.0:43.0
9c	toluene	(40)	55.0:45.0

		Catalyst, 0°		105, 265 105, 265 105

Catalyst	Solvent		er
$Rh_2(OAc)_4$	CH_2Cl_2	(77)	—
10b	CH_2Cl_2	(76)	72.5:27.5
10b	Et_2O	(56)	72.5:27.5

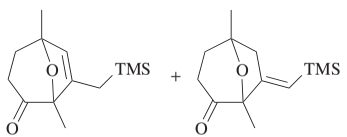
Catalyst



X	Catalyst	Solvent	Temp		er	
H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(87)	—	105, 264
H	**10b**	CH_2Cl_2	0°	(30)	53.5:46.5	105
H	**21**	CH_2Cl_2	0°	(17)	53.0:47.0	105
H	**9c**	CH_2Cl_2	0°	(27)	53.5:46.5	105
Cl	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(31)	—	105
Br	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(84)	—	105, 264
Br	**10b**	hexane	20°	(61)	61.5:38.5	105
Br	**10b**	CH_2Cl_2	20°	(56)	62.0:38.0	105
Br	**10b**	CH_2Cl_2	−10°	(42)	67.0:33.0	105, 264
Br	**21**	hexane	20°	(18)	55.0:45.0	105
Br	**21**	CH_2Cl_2	20°	(11)	54.0:46.0	105
Br	**8d**	toluene	20°	(39)	51.0:49.0	105
Br	**8d**	$PhCF_3$	20°	(44)	52.0:48.0	105
Br	**9c**	$PhCF_3$	0°	(22)	50.0:50.0	105

+ 10% allenyltrimethylsilane

$Rh_2(OAc)_4$, CH_2Cl_2, rt



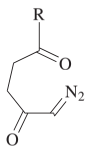
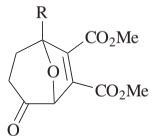
I **II**

I + **II** (82), **I**/**II** = 86:14

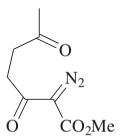
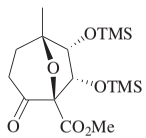
105

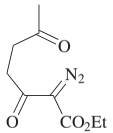
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

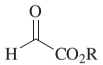
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-12} 		Catalyst, rt		

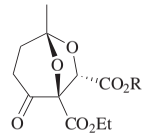
R	Catalyst	Solvent		er	
Et	**9c**	$PhCF_3$	(53)	92.0:8.0	97
$CH_2=CH(CH_2)_2$	$Rh_2(OAc)_4$	C_6H_6	(56)	—	43
$CH_2=CH(CH_2)_4$	$Rh_2(OAc)_4$	C_6H_6	(43)	—	43
$CH_2=CH(CH_2)_5$	$Rh_2(OAc)_4$	C_6H_6	(57)	—	43

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)		Refs.
C_7 		$Rh_2(OAc)_4$, C_6H_6, 70°		(16)	151



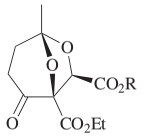


$Rh_2(OAc)_4$



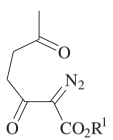
I

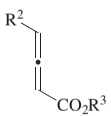
+



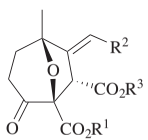
II

R	Solvent	Temp (°)	**I + II**	**I/II**	**I/II** (isolated)	
Et	CH_2Cl_2	rt	(50)	2.4:1	50:0	85
Et	toluene	110	(70)	2.5:1	60:10	85
Et	toluene	110	(60)	100:0	—	308
Et	toluene	rt	(49)	2:1	36:13	85
Et	C_6H_6	70	(87)	3:1	72:15	85
Et	C_6H_6	rt	(74)	3:1	54:20	85
Et	Et_2O	35	(54)	1.4:1	33:21	85
Et	hexane	70	(78)	1:1	43:35	85
Et	hexane	rt	(65)	1.7:1	47:18	85
t-Bu	toluene	110	(72)	3:1	61:11	85
t-Bu	hexane	70	(54)	3:1	46:8	85



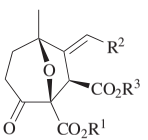


$Rh_2(OAc)_4$,
DCE/C_6H_6 (20:1), 65°



I

+



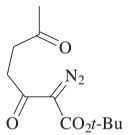
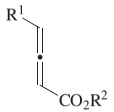
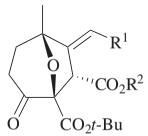
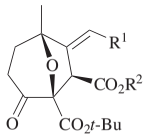
II

149

R^1	R^2	R^3	**I + II**	**I/II**
Et	H	Et	(64)	2.8:1
Et	H	Bn	(50)	2.7:1
Et	Me	Bn	(93)	3.0:1
Et	*n*-Pr	Et	(78)	>3:1
Et	*n*-Pr	Bn	(55)	>3:1
t-Bu	Bn	Bn	(78)	4.1:1

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

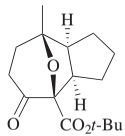
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C7 		Catalyst	 + 	149

I **II**

R^1	R^2	Catalyst	Solvent	Temp (°)	Time (h)	I + II	I/II
H	Et	$Rh_2(OAc)_4$	toluene	110	—	(82)	2.5:1
H	Et	$Rh_2(OAc)_4$	toluene	80	—	(80)	2.6:1
H	Et	$Rh_2(OAc)_4$	C_6H_6	80	—	(75)	2.6:1
H	Et	$Rh_2(OAc)_4$	C_6H_6	70	—	(74)	2.6:1
H	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	80	—	(80)	2.8:1
H	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	70	—	(82)	2.8:1
H	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	65	—	(85)	2.8:1
H	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	60	—	(5)	2.8:1
H	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	150 microwave (150 W)	—	(86)	2.8:1
H	Et	$Rh(oct)_4$	DCE/C_6H_6 (20:1)	65	—	(25)	2.8:1
H	Et	$Rh(oct)_4$	DCE/C_6H_6 (20:1)	150 microwave (150 W)	—	(45)	2.8:1
H	Et	$Rh_2(tfa)_4$	DCE/C_6H_6 (20:1)	65	—	(82)	2.8:1
H	Et	$Rh_2(tfa)_4$	DCE/C_6H_6 (20:1)	150 microwave (150 W)	—	(70)	2.8:1
H	Bn	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	150 microwave (150 W)	—	(88)	3.4:1
Me	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	65	—	(82)	2.8:1
Me	Bn	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	65	12	(90)	4.0:1
Me	Bn	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	150 microwave (150 W)	0.5	(90)	4.0:1
n-Pr	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	65	—	(72)	>3:1
n-Pr	Bn	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	65	—	(60)	>3:1
i-Pr	Bn	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	65	—	(50)	2.8:1
i-Bu	Bn	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	65	—	(53)	3.1:1
Bn	Et	$Rh_2(OAc)_4$	DCE/C_6H_6 (20:1)	150 microwave (150 W)	—	(88)	2.8:1

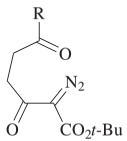
$Rh_2(OAc)_4$,rt



Solvent	
CH_2Cl_2	(14)
—	(26)

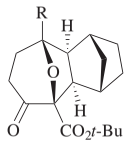
96, 309

C_{7-12}



x eq

Catalyst

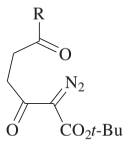
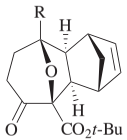


96, 309

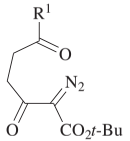
R	*x*	Catalyst	Solvent	Temp		er
Me	1.5	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(45)	—
Me	10	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(82)	—
Me	10	**10b**	hexane	rt	(83)	80.5:19.5
Me	10	**21**	hexane	rt	(74)	91.0:9.0
Me	10	**21**	hexane	0°	(62)	93.5:6.5
Me	10	**21**	hexane	−15°	(49)	96.0:4.0
Ph	—	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(53)	—
Ph	—	**10b**	hexane	rt	(59)	88.5:11.5
Ph	—	**10b**	hexane	0°	(54)	88.0:12.0
Ph	—	**21**	hexane	rt	(50)	75.5:24.5
Ph	—	**21**	hexane	0°	(48)	90.0:10.0
n-C_6H_{13}	—	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(76)	—
n-C_6H_{13}	—	**10b**	hexane	rt	(71)	85.0:15.0
n-C_6H_{13}	—	**21**	hexane	rt	(70)	89.5:10.5
n-C_6H_{13}	—	**21**	hexane	0°	(34)	91.0:9.0

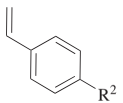
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

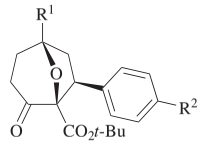
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-12} 	 *x* eq	Catalyst		96, 309

R	*x*	Catalyst	Solvent	Temp		er
Me	10	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(78)	—
Me	10	**9c**	hexane	rt	(65)	89.5:10.5
Me	10	**21**	hexane	0°	(53)	91.5:8.5
Ph	—	**10b**	hexane	rt	(59)	82.0:18.0
i-Pr	—	**10b**	hexane	0°	(31)	85.0:15.0
i-Pr	—	**10b**	hexane	rt	(51)	79.0:21.0
i-Pr	—	**21**	hexane	0°	(30)	81.5:18.5
i-Pr	—	**21**	hexane	rt	(28)	93.5:6.5
Ph	—	**10b**	hexane	0°	(27)	94.5:5.5
Ph	—	**21**	hexane	rt	(25)	88.5:11.5
Ph	—	**21**	hexane	0°	(41)	94.5:5.5
n-C_6H_{13}—		**10b**	hexane	rt	(53)	90.0:10.0
n-C_6H_{13}—		**21**	hexane	rt	(34)	70.5:29.5
n-C_6H_{13}—		**21**	hexane	0°	(35)	84.5:15.5





Catalyst



I

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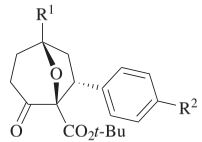


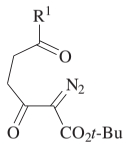
II

R^1	R^2	Catalyst	Solvent	Temp	**I + II**	**I/II**	er **I**	
Me	H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(53)	2:1	—	96
Me	H	**10b**	hexane	rt	(73)	10:1	80.5:19.5	96
Me	H	**21**	hexane	rt	(56)	2.5:1	61.0:39.0	96
Me	H	**21**	hexane	0°	(14)	—	81.0:19.0	96
Me	H	**8f**	$PhCF_3$	rt	(89)	100:0	98.5:1.5	48
Me	Cl	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(50)	2:1	—	96
Me	Cl	**10b**	hexane	rt	(60)	60:1	84.0:16.0	96
Me	Cl	**21**	hexane	rt	(49)	20:1	60.0:40.0	96
Me	MeO	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(43)	2:1	—	96
Me	MeO	**10b**	hexane	rt	(40)	100:0	90.5:9.5	96
Me	MeO	**21**	hexane	rt	(21)	100:0	77.5:22.5	96
Ph	H	**8d**	$PhCF_3$	rt	(50)	95:5	95.0:5.0	288a
Ph	H	**8d**	$PhCF_3$	60°	(36)	73:27	76.0:24.0	288a
Ph	H	**8f**	$PhCF_3$	rt	(85)	>99:1	99.5:0.5	48
Ph	H	**8f**	$PhCF_3$	60°	(88)	>99:1	97.5:2.5	288a
Ph	H	**8g**	$PhCF_3$	rt	(80)	>99:1	99.5:0.5	288a
Ph	H	**8g**	$PhCF_3$	60°	(86)	>99:1	96.5:3.5	288a
Ph	H	**8h**	$PhCF_3$	rt	(56)	>99:1	99.5:0.5	288a
Ph	H	**8i**	$PhCF_3$	rt	(64)	>99:1	99.5:0.5	288a
Ph	H	**8i**	$PhCF_3$	rt	(71)[j]	>99:1	99.5:0.5	288a

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

C_{7-12}



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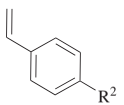
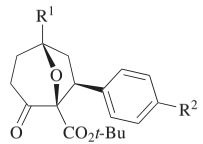


Catalyst



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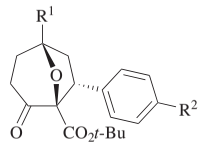
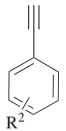
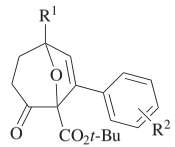


II

R^1	R^2	Catalyst	Solvent	Temp	**I + II**	**I/II**	er **I**	
Ph	H	**8j**	$PhCF_3$	rt	(69)	>99:1	99.5:0.5	288a
Ph	H	**8g**	$PhCF_3$	rt	(80)[j]	>99:1	99.5:0.5	288a
Ph	H	**8j**	$PhCF_3$	rt	(78)[j]	>99:1	99.5:0.5	288a



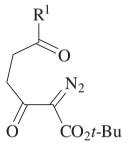
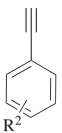
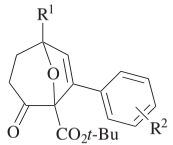
Catalyst



R^1	R^2	Catalyst	Solvent	Temp		er	
Me	H	$Rh_2(OAc)_4$	—	rt	(59)	—	96, 309
Me	H	**10b**	hexane	rt	(39)	69.0:31.0	96, 309
Me	H	**21**	hexane	rt	(41)	80.5:19.5	96, 309
Me	H	**18**	—	rt	(58)	78.0:22.0	96, 309
Me	H	**21**	—	rt	(86)	78.5:21.5	96, 309
Me	H	**8b**	$PhCF_3$	rt	(35)	85.0:15.0	48
Me	H	**8c**	$PhCF_3$	rt	(45)	90.0:10.0	48
Me	H	**8d**	$PhCF_3$	rt	(56)	94.5:5.5	48
Me	H	**8d**	$PhCF_3$	60°	(32)	78.0:22.0	48
Me	H	**8d**	$PhCF_3$	100°	(14)	64.0:36.0	48
Me	H	**9b**	$PhCF_3$	rt	(53)	87.5:12.5	48
Me	H	**9c**	$PhCF_3$	rt	(60)	91.0:9.0	48
Me	H	**9d**	$PhCF_3$	rt	(65)	93.5:6.5	48
Me	H	**8e**	$PhCF_3$	rt	(80)	96.0:4.0	48
Me	H	**8h**	$PhCF_3$	rt	(82)[h]	98.5:1.5	48
Me	H	**8i**	$PhCF_3$	rt	(55)[i]	95.5:4.5	288a
Me	H	**8f**	$PhCF_3$	60°	(80)	97.5:2.5	48
Me	H	**8f**	$PhCF_3$	100°	(70)	91.0:9.0	48

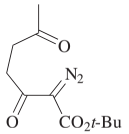
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

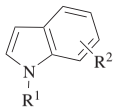
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-12}  (*Continued*)		Catalyst		

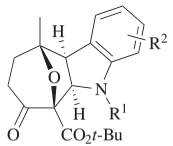
R^1	R^2	Catalyst	Solvent	Temp		er	Refs.
Me	H	**8f**	toluene	rt	(73)	97.5:2.5	48
Me	H	**8f**	C_6H_6	rt	(76)	95.5:4.5	48
Me	H	**8f**	hexanes	rt	(63)	95.0:5.0	48
Me	H	**8f**	Et_2O	rt	(23)	86.0:14.0	48
Me	H	**8f**	CH_2Cl_2	rt	(14)	70.0:30.0	48
Me	H	**8h**	$PhCF_3$	rt	(75)[j]	99.0:1.0	288a
Me	H	**8i**	$PhCF_3$	rt	(74)[j]	98.5:1.5	288a
Me	H	**8k**	$PhCF_3$	rt	(78)[j]	98.5:1.5	288a
Me	4-MeO	**8f**	$PhCF_3$	rt	(80)	99.0:1.0	48
Me	4-Me	**8f**	$PhCF_3$	rt	(77)	95.54.5	48
Me	4-Br	**8f**	$PhCF_3$	rt	(70)	98.5:1.5	48
Me	4-O_2N	**8f**	$PhCF_3$	rt	(17)	94.0:6.0	48
Me	3-MeO	**8f**	$PhCF_3$	rt	(64)	86.0:14.0	48
Me	2-MeO	**8f**	$PhCF_3$	rt	(53)	96.0:4.0	48
Ph	Ph	**8f**	$PhCF_3$	rt	(64)	96.0:4.0	48

C_7



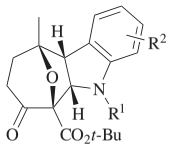


Catalyst



I

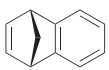
+



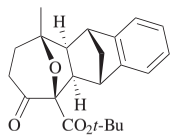
II

346

R^1	R^2	Catalyst	Solvent	Temp	**I** + **II**	**I/II**	er **I**	er **II**
H	H	**8f**	$PhCF_3$	60°	(49)	57:43	91.0:9.0	89.5:10.5
Me	H	$Rh_2(OAc)_4$	$PhCF_3$	rt	(57)	35:65	—	—
Me	H	**8f**	$PhCF_3$	rt	(81)	>99:1	99.5:0.5	—
Me	H	**8e**	$PhCF_3$	rt	(77)	>99:1	98.5:1.5	—
Me	H	**8d**	$PhCF_3$	rt	(71)	>99:1	94.5:5.5	—
Me	H	**8f**	toluene	rt	(75)	>99:1	96.5:3.5	—
Me	H	**8f**	CH_2Cl_2	rt	(33)	>99:1	93.5:6.5	—
Me	5-MeO	**8f**	$PhCF_3$	rt	(86)	>99:1	98.5:1.5	—
Me	5-Me	**8f**	$PhCF_3$	rt	(80)	>99:1	98.5:1.5	—
Me	5-Br	**8f**	$PhCF_3$	rt	(76)	>99:1	99.5:0.5	—
Me	4-Me	**8f**	$PhCF_3$	rt	(85)	>99:1	97.5:2.5	—
Me	7-Me	**8f**	$PhCF_3$	rt	(84)	>99:1	97.0:3.0	—



Catalyst

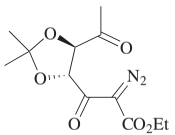
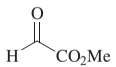
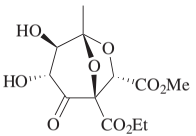
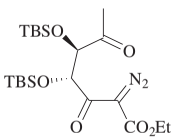
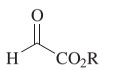
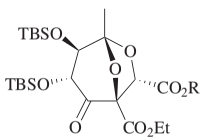
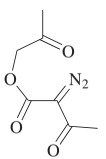
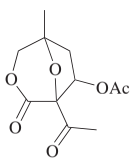
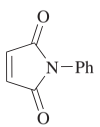
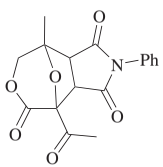


96

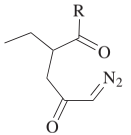
Catalyst	Solvent	Temp		er
$Rh_2(OAc)_4$	CH_2Cl_2	rt	(44)	—
10b	hexane	rt	(69)	87.0:13.0
21	hexane	rt	(66)	56.0:44.0
21	hexane	0°	(10)	53.0:47.0

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

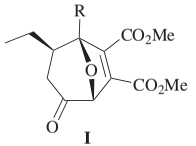
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. $Rh_2(OAc)_4$, toluene, 110° 2. $CDCl_3$, rt	 (>98)	85
		$Rh_2(OAc)_4$, toluene	 R: Me, Temp 80°, (42); *t*-Bu, Temp 110°, (58)	85
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (75)	291
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (94)	162, 291

C_{8-13}

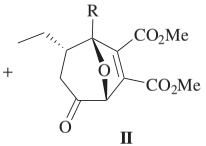


Catalyst, rt



I

+

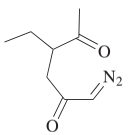


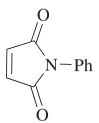
II

310

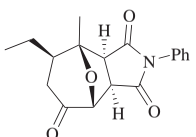
R	Catalyst	Solvent	**I + II**	**I/II**
Me	**1a**	CH_2Cl_2	(86)	2.5:1
Me	**1a**	toluene	(82)	2.2:1
Me	**1a**	Et_2O	(—)	—
Me	$Rh_2(OAc)_4$	CH_2Cl_2	(84)	2.7:1
Me	**1d**	CH_2Cl_2	(83)	2.2:1
Me	**1f**	CH_2Cl_2	(74)	1.5:1
Me	$Rh_2(cap)_4$	CH_2Cl_2	(87)	2.6:1
Me	$Rh_2(pfb)_4$	CH_2Cl_2	(82)	2.5:1
i-Pr	**1a**	CH_2Cl_2	(74)	1:3.6
i-Pr	$Rh_2(OAc)_4$	CH_2Cl_2	(81)	2.3:1
Ph	**1a**	CH_2Cl_2	(84)	100:0
Ph	$Rh_2(OAc)_4$	CH_2Cl_2	(74)	100:0

C_8



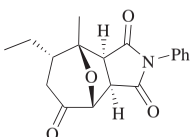


Catalyst, CH_2Cl_2, rt



I

+



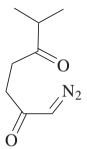
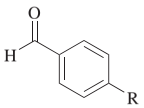
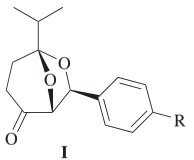
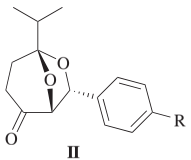
II

310

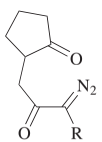
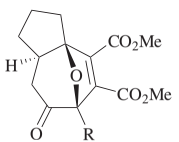
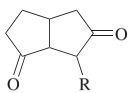
Catalyst	**I + II**	**I/II**
1a	(82)	1:1.8
$Rh_2(OAc)_4$	(80)	1:1.4

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		Catalyst **9c**, $PhCF_3$, rt	 **I** +  **II**	311

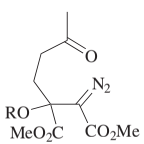
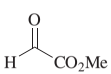
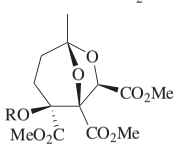
R	I + II	I/II	er I
H	(62)	91:9	89.5:10.5
O_2N	(63)	93:7	65.0:35.0
MsO	(72)	95:5	87.0:13.0
AcO	(63)	94:6	88.5:11.5
MeO	(57)	94:6	93.5:6.5
MOMO	(60)	94:6	93.5:6.5
BnO	(64)	95:5	93.0:7.0

C_{8-9} 		$Rh_2(OAc)_4$, C_6H_6	 **I** +  **II**	

R	Temp	I	II
H	rt	(60)	(30)
EtO_2C	80°	(89)	(0)

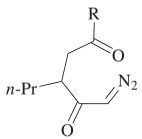
45

163

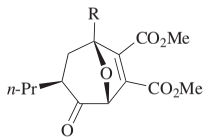
C_8 		$Rh_2(OAc)_4$, toluene, reflux		83, 84

R		dr
TMS	(54)	8:1
TBS	(64)	10:1

C_{9-14}



Catalyst, CH_2Cl_2, rt



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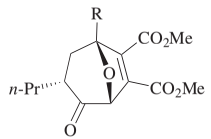
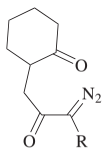


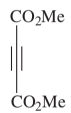
310

I **II**

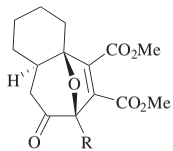
R	Catalyst	**I** + **II**	**I**/**II**
Me	**1a**	(80)	1:1.8
Me	$Rh_2(OAc)_4$	(88)	1:1.7
Ph	**1a**	(80)	1:1.1
Ph	$Rh_2(OAc)_4$	(51)	1:1.4

C_{9-10}





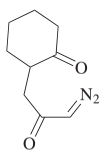
$Rh_2(OAc)_4$

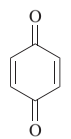


R	Solvent	Temp	
H	CH_2Cl_2	rt	(71)
EtO_2C	C_6H_6	80°	(86)

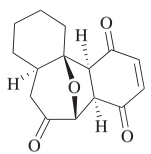
163

C_9





$Rh_2(OAc)_4$, CH_2Cl_2, rt



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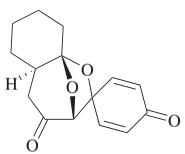
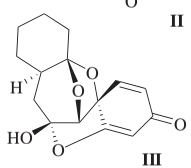


302

I **II**

+



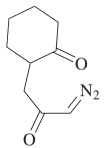
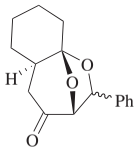
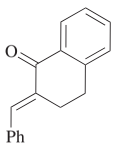
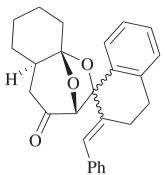
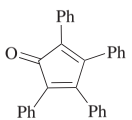
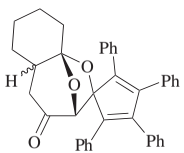
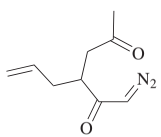
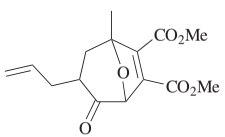
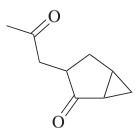
III

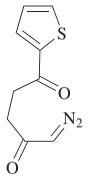
I + **II** + **III** (45)

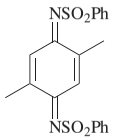
I/**II**/**III** = 5:15:25

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

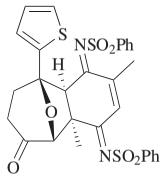
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (63) dr 2:1	176
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (51) dr 3:2	181
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (59) dr 3:1	176
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (47) +  (33)	249



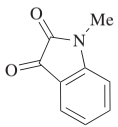


$Rh_2(OAc)_4$, C_6H_6, rt

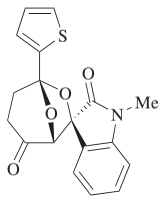


(53)

296

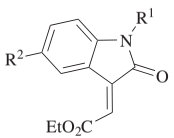


$Rh_2(OAc)_4$, toluene, rt

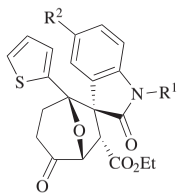


(44)

297



$Rh_2(OAc)_4$, toluene, rt



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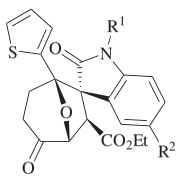


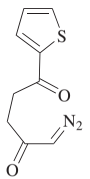
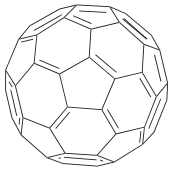
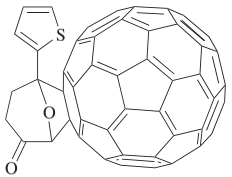
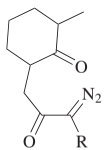
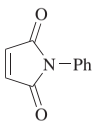
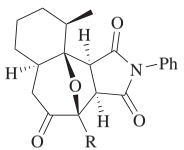
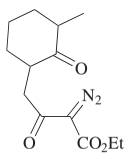
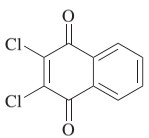
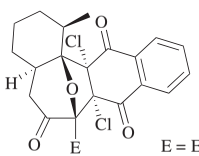
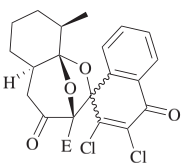
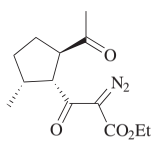
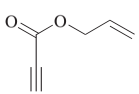
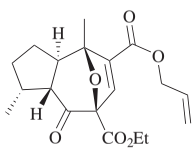
298

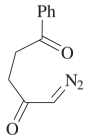
I **II**

R^1	R^2	**I + II**	**I/II**
H	H	(95)	2:1
H	Br	(70)	2:1
Me	H	(95)	2:1
Bn	H	(88)	1.1:1

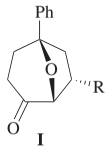
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Rh_2(OAc)_4$, toluene, rt	 (53)	146
C_{10-11} 		$Rh_2(OAc)_4$	 R Solvent Temp H CH_2Cl_2 rt (69) EtO_2C C_6H_6 80° (92)	163
C_{11} 		$Rh_2(OAc)_4$, C_6H_6, 80°	 +  E = EtO_2C **I** **II** **I** + **II** (45), **I**/**II** = 5:40	302
		$Rh_2(OAc)_4$, toluene	 Temp (°) Time (h) 60 12 (50) 80 1 (80) 100 0.25 (100)	312

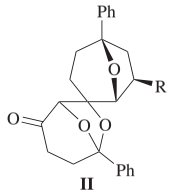


$Rh_2(OAc)_4$, C_6H_6, rt



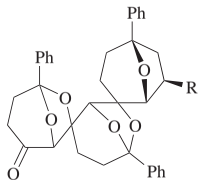
I

+



II

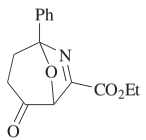
+ 45



III

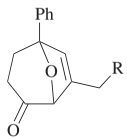
R	**I** + **II** + **III**	**I**/**II**/**III**
AcO	(85)	70:0:15
EtO	(56)	28:16:12

$Rh_2(OAc)_4$, CH_2Cl_2, rt



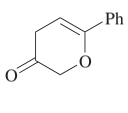
(85) 45

Catalyst, rt



I

+

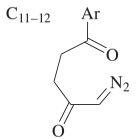
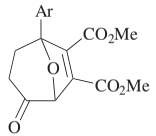


II

R	Catalyst	Solvent	**I**	**II**	
Cl	$Rh_2(OAc)_4$	C_6H_6	(85)	(0)	45
Br	**1a**	CH_2Cl_2	(14)	(56)	171
MeO	$Rh_2(OAc)_4$	C_6H_6	(85)	(0)	45

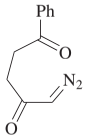
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

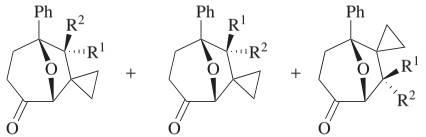
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst		

Ar	Catalyst	Solvent	Temp		er	Refs.
Ph	$Rh_2(OAc)_4$	C_6H_6	rt	(93)	—	45, 290
Ph	$Rh_2(OAc)_4$	[bmim]BF_4	rt	(95)	—	190
Ph	**1a**	CH_2Cl_2	rt	(85)	—	171
Ph	**8a**	$PhCF_3$	rt	(81)	80.0:20.0	97
Ph	**8a**	C_6H_6	rt	(64)	79.5:20.5	97
Ph	**8a**	PhF	rt	(70)	79.0:21.0	97
Ph	**8a**	CH_2Cl_2	rt	(79)	60.0:40.0	97
Ph	**8a**	Et_2O	rt	(63)	64.5:35.5	97
Ph	**8b**	$PhCF_3$	rt	(79)	80.5:19.5	97
Ph	**8c**	$PhCF_3$	rt	(79)	79.5:20.5	97
Ph	**8d**	$PhCF_3$	rt	(80)	84.5:15.5	97
Ph	**9a**	$PhCF_3$	rt	(81)	91.0:9.0	97
Ph	**9b**	$PhCF_3$	rt	(79)	91.5:8.5	97
Ph	**9c**	$PhCF_3$	rt	(79)	95.0:5.0	97
Ph	**9d**	$PhCF_3$	rt	(83)	82.5:17.5	97
Ph	**9c**	$PhCF_3$	0°	(77)	95.0:5.0	97
Ph	**9c**	$PhCF_3$	−23°	(54)	96.0:4.0	97
4-ClC_6H_4	**9c**	$PhCF_3$	0°	(78)	93.5:6.5	97
4-$MeOC_6H_4$	**9c**	$PhCF_3$	0°	(65)	95.0:5.0	97
4-MeC_6H_4	**9c**	$PhCF_3$	0°	(67)	96.0:4.0	97
4-$CF_3C_6H_4$	**9c**	$PhCF_3$	0°	(65)	91.5:8.5	97

C_{11}



$Rh_2(OAc)_4$, CH_2Cl_2, 20°



I + **II** + **III**

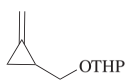
147

R^1	R^2	**I**	**II**	**III**
Br	H	(14)	(16)	(0)
MeO_2C	Cl	(30)	(15)	(0)
Ph	H	(6)	(33)	(10)
n-C_7H_{15}	H	(9)	(9)	(8)

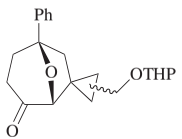
$Rh_2(OAc)_4$, CH_2Cl_2, 20°

(28) + (29)

147



$Rh_2(OAc)_4$, CH_2Cl_2, 20°

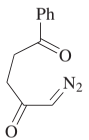
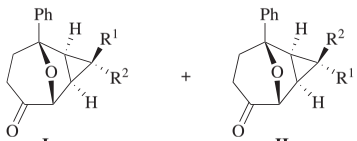


(42)

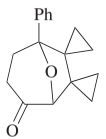
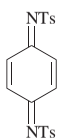
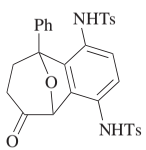
147

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

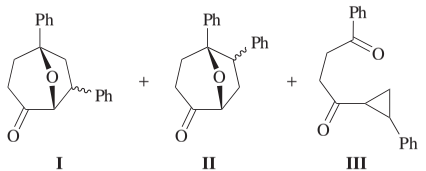
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
	 *x* eq	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** + **II**	148

R^1	R^2	*x*	**I**	**II**
Me	Me	3	(68)	(—)
Me	Me	5	(80)	(—)
Ph	Ph	3	(58)	(—)
Me	Ph	3	(46)	(17)
Me	MeO_2C	3	(12)	(—)
Me	MeO_2C	5	(36)	(—)

		$Rh_2(OAc)_4$, CH_2Cl_2, 20°	 (57)	147
		$Rh_2(OAc)_4$, C_6H_6, rt	 (51)	296

Catalyst **1a**, CH_2Cl_2, rt

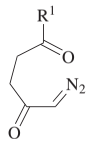


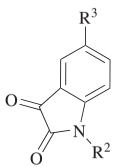
I + **II** + **III** (83), **I**/**II**/**III** = 24.5:3.5:55

exo/*endo* **I** 26:1, *exo*/*endo* **II** 5:1

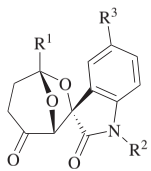
171

$C_{11–15}$





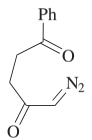
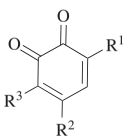
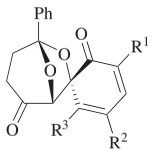
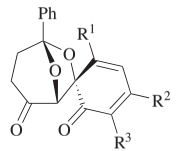
$Rh_2(OAc)_4$, toluene, rt



R^1	R^2	R^3		
Ph	H	H	(79)	297
Ph	H	Br	(70)	297
Ph	Me	H	(83)	297, 313
Ph	Ph	H	(75)	297, 313
Ph	Bn	H	(78)	297, 313
4-ClC_6H_4	Me	H	(80)	297
4-$MeOC_6H_4$	Ph	H	(69)	297
4-MeC_6H_4	Ph	H	(68)	297
Fc	Ph	H	(57)	297

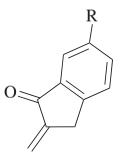
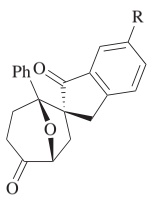
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

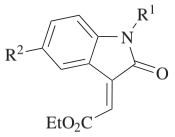
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		$Rh_2(OAc)_4$, toluene, rt	 +  + 2:1 adduct **III**	

I **II**

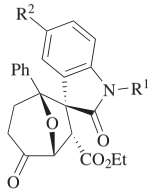
R^1	R^2	R^3	**I**	**II**	**III**	Refs.
H	Me	Me	(48)	(—)	(—)	313
H	*t*-Bu	H	(42)	(—)	(15)	313
H	*t*-Bu	H	(55)	(—)	(—)	299
H	*t*-Bu	MeO	(48)	(—)	(—)	299, 314
t-Bu	*t*-Bu	H	(76)	(—)	(—)	299, 314
t-Bu	*t*-Bu	MeO	(63)	(—)	(—)	299, 313
						314
Ph_2CH	Ph_2CH	MeO	(41)	(—)	(15)	313, 314
Ph_2CH	Ph_2CH	MeO	(37)	(40)	(—)	299

		$Rh_2(OAc)_4$, CH_2Cl_2, rt		

R		Refs.
H	(76)	169
Br	(90)	
MeOCHN	(82)	

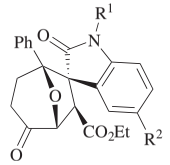


$Rh_2(OAc)_4$, toluene, rt



I

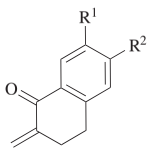
+



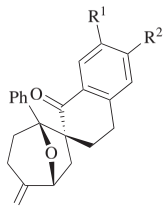
II

298

R^1	R^2	**I + II**	**I/II**
H	H	(98)	1.1:1
H	Br	(97)	2:1
Me	H	(87)	2:1
Bn	H	(89)	2:1



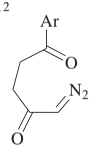
$Rh_2(OAc)_4$, CH_2Cl_2, rt

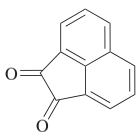


R^1	R^2	
MeOCHN	H	(55)
H	MeO	(30)

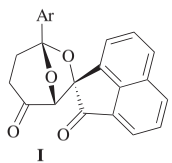
169

C_{11-12}



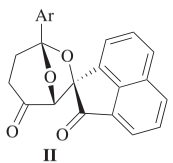


$Rh_2(OAc)_4$, toluene, rt



I

+



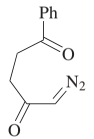
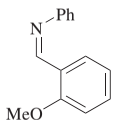
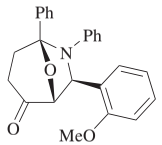
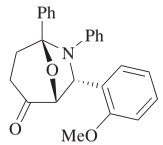
II

299, 313

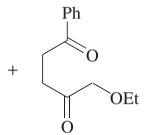
Ar	**I + II**	**I/II**
Ph	(67)	1.3:1
4-$MeOC_6H_4$	(61)	1:1.6
4-MeC_6H_4	(68)	2.8:1

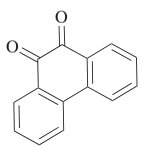
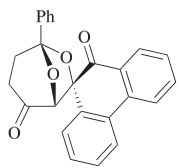
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

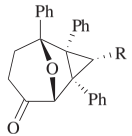
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		$Rh_2(OAc)_4$, L.A. (10 mol %), 4 Å MS	 +  **I** **II**	44

L.A.	Solvent	Temp	I + II	I/II	III
$Sc(OTf)_3$	CH_2Cl_2	rt	(34)	89:11	(—)
$Sc(OTf)_3$	Et_2O	rt	(21)	97:3	(8)
$Tm(OTf)_3$	CH_2Cl_2	rt	(28)	81:19	(—)
$Tm(OTf)_3$	Et_2O	rt	(19)	93:7	(7)
$Yb(OTf)_3$	CH_2Cl_2	rt	(28)	88:12	(—)
$Yb(OTf)_3$	CH_2Cl_2	reflux	(29)	90:10	(—)
$Yb(OTf)_3$	toluene	80°	(trace)	85:15	(—)
$Yb(OTf)_3$	Et_2O	rt	(39)	99:1	(12)
$Yb(OTf)_3$	*t*-BuOMe	rt	(trace)	81:19	(—)


III

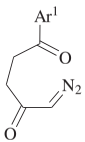
	$Rh_2(OAc)_4$, toluene, rt		(37)		313, 314

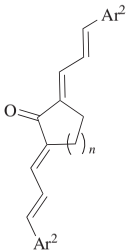
$Rh_2(OAc)_4$, CH_2Cl_2, rt



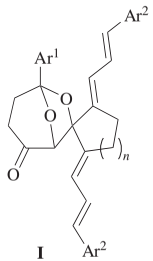
R		
H	(84)	148, 315
Me	(83)	148, 315
CH_2=CH	(71)	148, 315
(*Z*)-PhCH=CH	(69)	315
Ph	(68)	148, 315

C_{11-15}



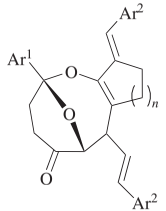


1. $Rh_2(OAc)_4$, CH_2Cl_2, rt
2. Al_2O_3 chromatography



I

+

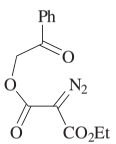


II

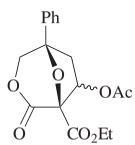
180

n	Ar^1	Ar^2	**I**	**II**
1	Ph	Ph	(trace)	(36)
1	Ph	2-$MeOC_6H_4$	(10)	(42)
1	4-$MeOC_6H_4$	2-$MeOC_6H_4$	(trace)	(28)
1	4-MeC_6H_4	2-$MeOC_6H_4$	(trace)	(34)
1	1-naphthyl	2-$MeOC_6H_4$	(trace)	(32)
2	Ph	2-$MeOC_6H_4$	(44)	(—)

C_{11}



$Rh_2(OAc)_4$, C_6H_6, 80°



(—)

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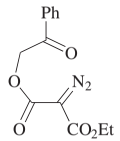
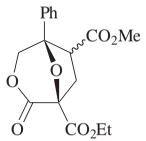
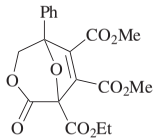
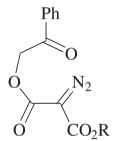
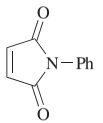
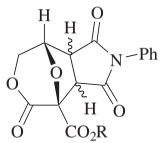
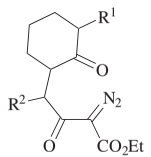
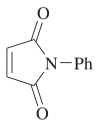
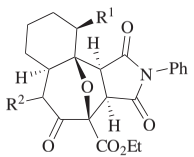
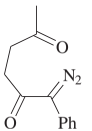
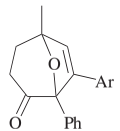
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		$Rh_2(OAc)_4$, C_6H_6, 80°	 (—)	162
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (66)	162, 291
		$Rh_2(OAc)_4$, C_6H_6, 90°	 R: Et (75); CH_2=$CHCH_2$ (58)	162, 291
C_{12} 		$Rh_2(OAc)_4$, C_6H_6, 80°	 R^1 R^2: Et H (93); Me Me (84)	163



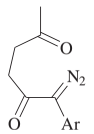
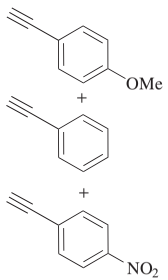
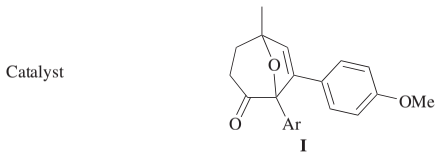
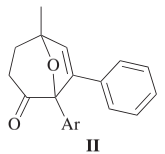
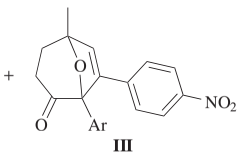
Catalyst



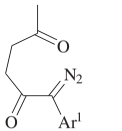
Ar	Catalyst	Solvent	Temp		er	
Ph	—	—	reflux	(2)	—	46
Ph	$Rh_2(OAc)_4$	—	rt	(60)	—	46
Ph	$Rh_2(OAc)_4$	toluene	rt	(60)	—	46, 182
Ph	**10b**	CH_2Cl_2	rt	(15)	51.5:48.5	46
Ph	**10b**	toluene	rt	(29)	52.5:47.5	46
Ph	**18**	—	rt	(25)	69.0:31.0	46
Ph	**18**	CH_2Cl_2	rt	(25)	51.5:48.5	46
Ph	**18**	toluene	rt	(37)	69.0:31.0	46, 182
Ph	**9c**	—	rt	(39)	68.0:32.0	46
Ph	**9c**	$PhCF_3$	rt	(47)	64.0:36.0	46, 182
4-$MeOC_6H_4$	—	toluene	reflux	(8)	—	46
4-$MeOC_6H_4$	$Rh_2(OAc)_4$	toluene	rt	(76)	—	46, 182
4-$MeOC_6H_4$	**18**	CH_2Cl_2	rt	(22)	51.5:48.5	46
4-$MeOC_6H_4$	**18**	toluene	rt	(41)	55.0:45.0	46, 182
4-$MeOC_6H_4$	**9c**	$PhCF_3$	rt	(43)	51.5:48.5	46, 182
4-$O_2NC_6H_4$	—	toluene	reflux	(8)	—	46
4-$O_2NC_6H_4$	$Rh_2(OAc)_4$	toluene	rt	(60)	—	46, 182
4-$O_2NC_6H_4$	**18**	CH_2Cl_2	rt	(43)	62.0:38.0	46
4-$O_2NC_6H_4$	**18**	toluene	rt	(50)	65.5:34.5	46, 182
4-$O_2NC_6H_4$	**9c**	$PhCF_3$	rt	(73)	50.5:49.5	46, 182

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

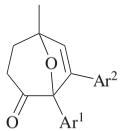
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	 1:1:1	Catalyst  **I** +  **II** +  **III**		46, 182

Ar	Catalyst	Solvent	Temp	**I/II/III**
Ph	—	toluene	reflux	1:1:4
Ph	$Rh_2(OAc)_4$	toluene	rt	1:1:9
Ph	**18**	toluene	rt	1.5:1:8
Ph	**9c**	$PhCF_3$	rt	1:1:11
4-$O_2NC_6H_4$	—	toluene	reflux	2.5:1:2
4-$O_2NC_6H_4$	$Rh_2(OAc)_4$	toluene	rt	1.5:1:1
4-$O_2NC_6H_4$	**18**	toluene	rt	2:1:1
4-$O_2NC_6H_4$	**9c**	$PhCF_3$	rt	2.5:1:2.5



$Ar^1 = 4\text{-}O_2NC_6H_4$

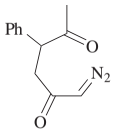
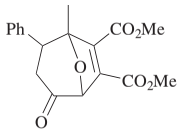
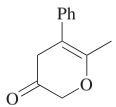
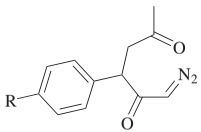
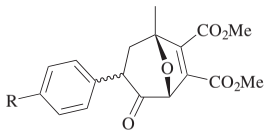
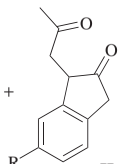
Catalyst



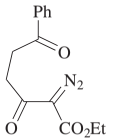
Ar^2	Catalyst	Solvent	Temp		er	
Ph	—	toluene	reflux	(19)	—	46
Ph	$Rh_2(OAc)_4$	—	rt	(98)	—	46
Ph	$Rh_2(OAc)_4$	toluene	rt	(82)	—	46, 182
Ph	**10b**	CH_2Cl_2	rt	(34)	51.0:49.0	46
Ph	**10b**	toluene	rt	(34)	51.5:48.5	46
Ph	**18**	—	rt	(73)	83.0:17.0	46, 182
Ph	**18**	CH_2Cl_2	rt	(22)	64.5:35.5	46
Ph	**18**	toluene	rt	(54)	74.0:26.0	46, 182
Ph	**21**	—	rt	(80)	83.0:17.0	46, 182
Ph	**21**	—	0°	(83)	88.0:12.0	46, 182
Ph	**9c**	—	rt	(49)	72.5:27.5	46
Ph	**9c**	$PhCF_3$	rt	(69)	71.5:28.5	46, 182
$4\text{-}MeOC_6H_4$	—	toluene	reflux	(17)	—	46
$4\text{-}MeOC_6H_4$	$Rh_2(OAc)_4$	toluene	rt	(89)	—	46, 182
$4\text{-}MeOC_6H_4$	**18**	CH_2Cl_2	rt	(41)	50.0:50.0	46
$4\text{-}MeOC_6H_4$	**18**	toluene	rt	(48)	59.0:41.0	46, 182
$4\text{-}MeOC_6H_4$	**9c**	$PhCF_3$	rt	(65)	70.0:30.0	46, 182
$4\text{-}O_2NC_6H_4$	**—**	toluene	reflux	(17)	—	46
$4\text{-}O_2NC_6H_4$	$Rh_2(OAc)_4$	toluene	rt	(82)	—	46, 182
$4\text{-}O_2NC_6H_4$	**18**	CH_2Cl_2	rt	(26)	67.5:32.5	46
$4\text{-}O_2NC_6H_4$	**18**	toluene	rt	(33)	65.5:34.5	46, 182
$4\text{-}O_2NC_6H_4$	**9c**	$PhCF_3$	rt	(72)	69.0:31.0	46, 182

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

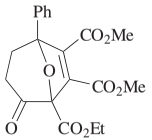
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
		$Rh_2(cap)_4$, CH_2Cl_2	 (22) +  (78)	H10
		Catalyst	 **I** +  **II**	

R	Catalyst	Solvent	Temp	**I + II**	**I/II**	
H	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(80)	60:20	249
H	$Rh_2(OAc)_4$	C_6H_6	rt	(80)	75:25	65
H	$Rh_2(cap)_4$	CH_2Cl_2	45°	(90)	100:0	249
H	$Rh_2(cap)_4$	C_6H_6	rt	(90)	100:0	65
H	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(85)	0:100	249
H	$Rh_2(pfb)_4$	C_6H_6	rt	(85)	0:100	65
MeO	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(83)	72:11	249
MeO	$Rh_2(OAc)_4$	C_6H_6	rt	(80)	75:25	65
MeO	$Rh_2(cap)_4$	CH_2Cl_2	45°	(66)	100:0	249
MeO	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(47)	0:100	249
MeO	$Rh_2(pfb)_4$	C_6H_6	rt	(85)	0:100	65

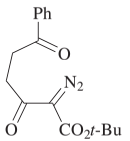


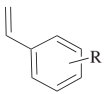
$Rh_2(OAc)_4$, C_6H_6, 75°



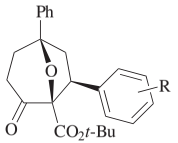
(91)

45



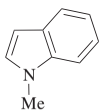


Catalyst **8f**, $PhCF_3$, rt

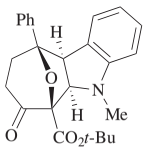


R		er
4-Br	(80)	99.5:0.5
2-MeO	(75)	99.5:0.5
3-MeO	(88)	99.0:1.0
4-MeO	(94)	99.5:0.5
4-Me	(90)	99.0:1.0
4-CF_3	(73)	95.0:5.0

48



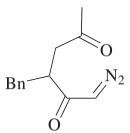
Catalyst **8f**, $PhCF_3$, rt



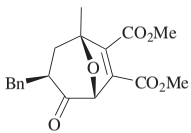
(83) er 98.5:1.5

346

C_{13}

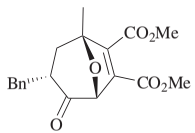


Catalyst, CH_2Cl_2, rt



I

+

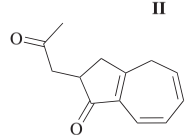


II

310

Catalyst	**I + II**	**I/II**	**III**
1a	(83)	1:1.7	(—)
$Rh_2(OAc)_4$	(57)	1:1.9	(28)

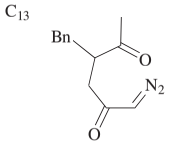
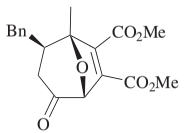
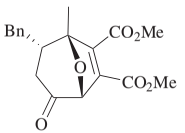
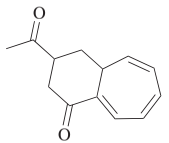
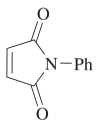
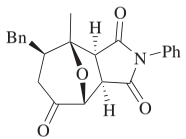
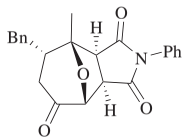
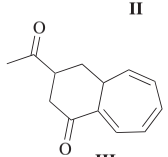
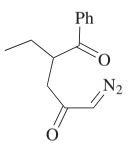
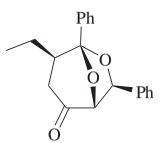
+



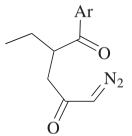
III

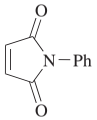
TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

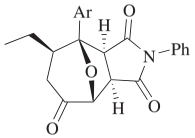
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst, CH_2Cl_2, rt	 **I** +  **II**	310
			Catalyst **I + II** **I/II** **III** **1a** (84) 1.7:1 (—) $Rh_2(OAc)_4$ (74) 2.5:1 (<10) +  **III**	
		Catalyst, CH_2Cl_2, rt	 **I** +  **II**	310
			Catalyst **I + II** **I/II** **III** **1a** (83) 1.5:1 (—) $Rh_2(OAc)_4$ (57) 1:1.2 (<11) +  **III**	
		Catalyst, CH_2Cl_2, rt		310
			Catalyst **1a** (71) $Rh_2(OAc)_4$ (79)	

$C_{13–14}$



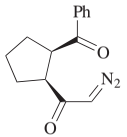


Catalyst, CH_2Cl_2, rt

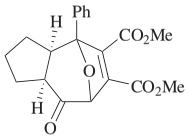


Ar	Catalyst		
Ph	**1a**	(81)	
Ph	$Rh_2(OAc)_4$	(82)	310
4-$MeOC_6H_4$	**1a**	(70)	
4-$MeOC_6H_4$	$Rh_2(OAc)_4$	(73)	
4-$CF_3C_6H_4$	**1a**	(88)	
4-$CF_3C_6H_4$	$Rh_2(OAc)_4$	(86)	

C_{14}

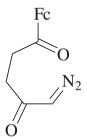


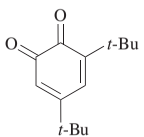
$Rh_2(OAc)_4$, C_6H_6, rt



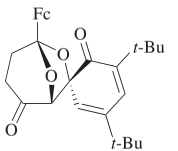
(75) 109

C_{15}





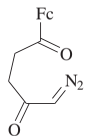
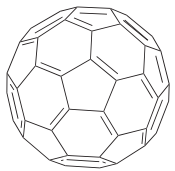
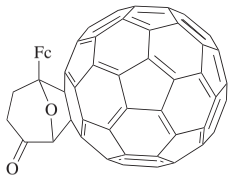
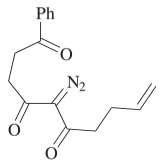
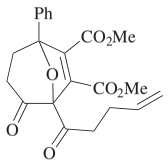
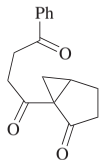
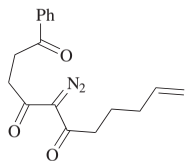
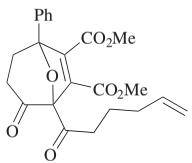
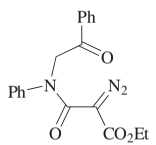
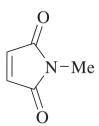
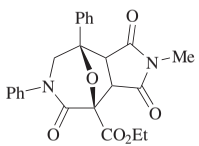
$Rh_2(OAc)_4$, toluene, rt

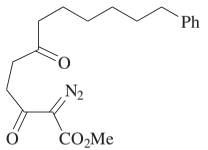
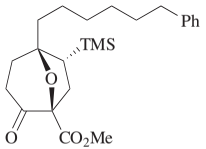
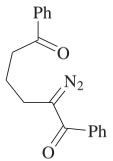
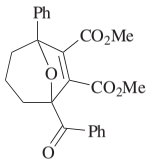
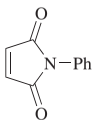
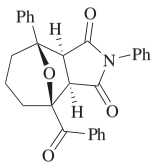


(42) 299

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

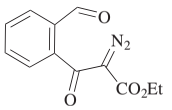
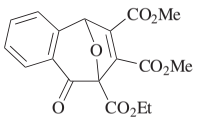
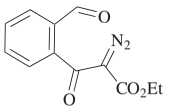
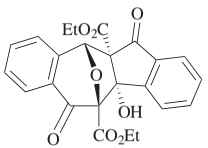
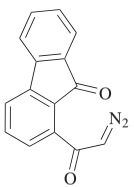
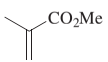
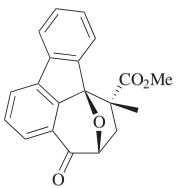
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}				
		$Rh_2(OAc)_4$, toluene, rt	 (40)	145, 146
C_{16}				
		$Rh_2(OAc)_4$, C_6H_6, 60°	 (68) +  (15)	43
C_{17}				
		$Rh_2(OAc)_4$, C_6H_6, 60°	 (46)	43
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (64)	316

C_{18} 		$Rh_2(OAc)_4$, C_6H_6, 70°		(47)	151
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		(89)	120
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		(90)	120

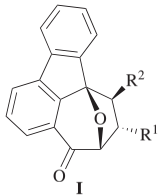
[a] The reaction was carried out by adding a solution of the diazo compound to a suspension of dipolarophile, catalyst, and 4 Å MS, over a period of 1 hour.
[b] The reaction was carried out by adding a solution of the diazo compound and dipolarophile to a suspension of catalyst and 4 Å MS, over a period of 1 hour.
[c] Dried and purified CH_2Cl_2 (via distillation with $CaCl_2$, then CaH_2) was used.
[d] Dried and purified toluene (typical procedures) was used.
[e] The reaction was carried out in dried and purified CH_2Cl_2 with MeOH (10 mol %) as an additive.
[f] The reaction was carried out using 20 mol % catalyst.
[g] The reaction was carried out using 50 mol % catalyst.
[h] The reaction was carried out using 1 mol % catalyst.
[i] The reaction was carried out using 0.1 mol % catalyst.
[j] The reaction was carried out using continuous flow conditions.
[k] The reaction was carried out using 0.0067 mol % catalyst.

TABLE 10. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM KETONES (*Continued*)

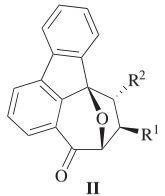
B. PYRYLIUMS

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		$Rh_2(tfa)_4$, CH_2Cl_2, 40°	 (82)	119
		$Rh_2(OAc)_4$, CH_2Cl_2, 40°	 (63)	119
C_{15}				
		$Cu(acac)_2$, C_6H_6, 80°	 (88)	216

$Cu(acac)_2$, C_6H_6, 80°



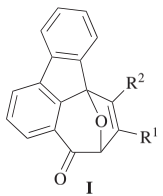
+



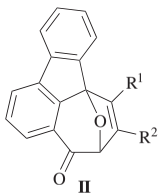
216

R^1	R^2	**I**	**II**
H	Ph	(79)	(—)
MeO_2C	MeO_2C	(34)	(54)
MeO_2C	Ph	(66)	(—)
MeO_2C	4-BrC_6H_4	(66)	(—)
Ph	Ph	(26)	(—) + dimer (70)
Bz	Bz	(92)	(—)

$Cu(acac)_2$, C_6H_6, 80°



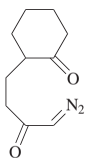
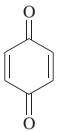
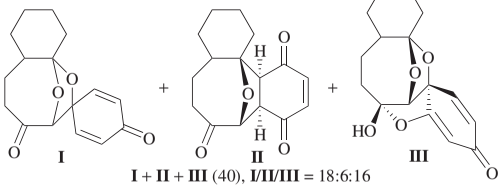
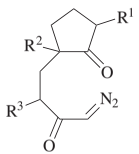
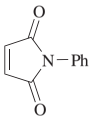
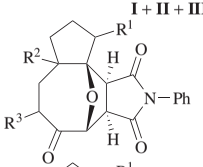
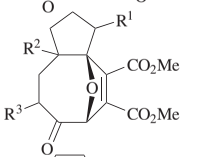
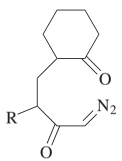
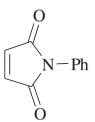
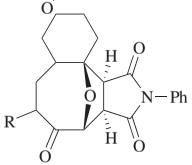
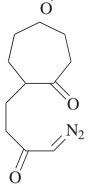
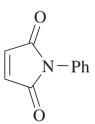
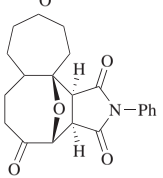
+



216

R^1	R^2	**I**	**II**
H	MeO_2C	(80)	(—)
H	Ph	(86)	(—)
MeO_2C	MeO_2C	(100)	(—)
MeO_2C	Ph	(30)	(24)
Bz	Bz	(89)	(—)

TABLE 11. INTERMOLECULAR CYCLOADDITIONS OF 7-MEMBERED-RING CARBONYL YLIDES FROM KETONES

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*				
C_{10} 		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 **I** + **II** + **III** (40), **I/II/III** = 18:6:16	110
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		110
C_{10-11}		$Rh_2(OAc)_4$, CH_2Cl_2, rt		110
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		110
C_{11} 		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (64)	110

R^1	R^2	R^3	
H	H	Me	(61)
H	Me	H	(49)
Me	H	H	(58)

R^1	R^2	R^3	
H	H	Me	(54)
H	Me	H	(45)
Me	H	H	(61)

R	
H	(57)
Me	(58)

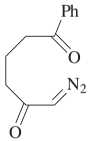
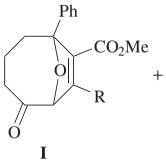
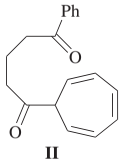
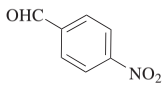
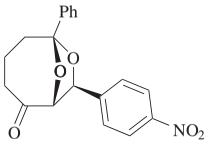
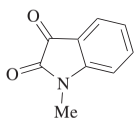
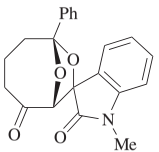
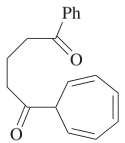
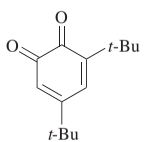
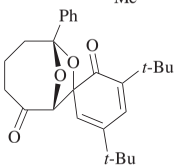
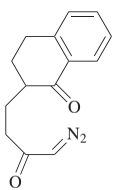
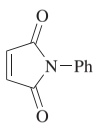
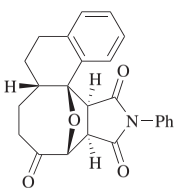
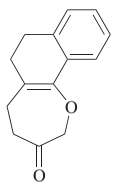
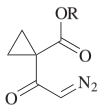
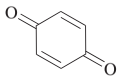
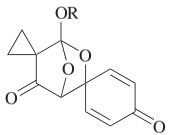
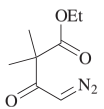
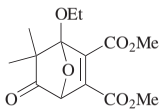
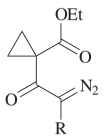
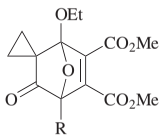
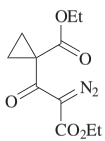
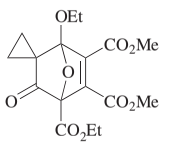
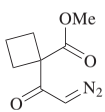
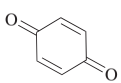
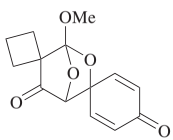
C_{12} 		$Rh_2(OAc)_4$, C_6H_6, rt	 **I** +  **II**	R: H; MeO_2C	**I**: (43); (45)	**II**: (24); (22)	112, 113
		Catalyst **9c**, $PhCF_3$, 0°		(60)	er 89.5:10.5		99
		$Rh_2(OAc)_4$, C_6H_6, rt		(32)	+ 	(8)	297
		$Rh_2(OAc)_4$, toluene, rt		(37)			299
C_{14} 		$Rh_2(OAc)_4$, CH_2Cl_2, rt		(40)	+ 	(13)	110

TABLE 12. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM ESTERS OR ANHYDRIDES

A. NON-AROMATIC YLIDES

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		$Rh_2(OCOC_6H_4\text{-}3\text{-}Cl)_4$, 1,2-$Me_2C_6H_4$, 80°	 R: Me (76); Et (74)	166
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (85)[a]	112
C_{6-7} 		$Rh_2(OAc)_4$, C_6H_6, 80°	 R: H (55)[b]; EtO_2C (68)	112; 155, 157
C_7 		1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. Dipolarophile, 80°	 (58)	155, 157
		$Rh_2(OCOC_6H_4Cl\text{-}3)_4$, 1,2-$Me_2C_6H_4$, 80°	 (76)	166

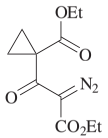
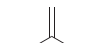
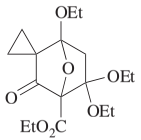
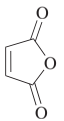
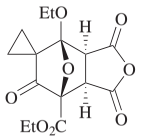
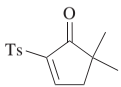
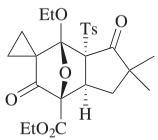
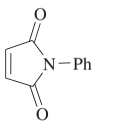
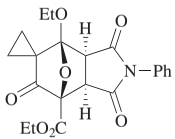
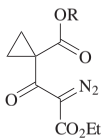
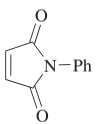
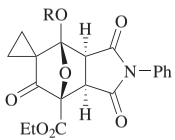
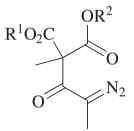
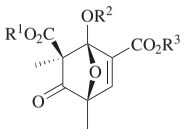
		$Rh_2(OAc)_4$, C_6H_6, 80°		(68)	155, 157
		$Rh_2(OAc)_4$, C_6H_6, 80°		(69)	155, 157
		$Rh_2(OAc)_4$, C_6H_6, 80°		(60)	157
		$Rh_2(OAc)_4$, C_6H_6, 80°		(68)	155, 157
		1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. Dipolarophile, 80°		R Et (61) CH_2=CH(CH_2)$_3$ (38)	155, 157 157

TABLE 12. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM ESTERS OR ANHYDRIDES (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

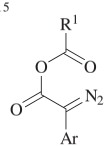
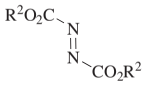
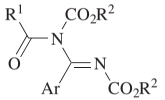
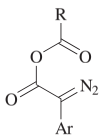
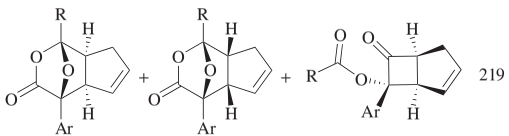
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		Catalyst, C_6H_6		186

R^1	R^2	R^3	Catalyst	Temp (°)	
Me	Me	Me	$Rh_2(pfb)_4$	80	(75)
$TMS(CH_2)_2$	$TMSCH_2$	Me	$Rh_2(OAc)_4$	60	(75)
$TMS(CH_2)_2$	$TMSCH_2$	CH_2=$CHCH_2$	$Rh_2(OAc)_4$	60	(73)

[a] A yield of 74% was given in the experimental section.

[b] A yield of 48% was given in the experimental section.

TABLE 12. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM ESTERS OR ANHYDRIDES
B. 1,3-DIOXOLIUMS

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-15}  Ar = 4-$O_2NC_6H_4$		$Rh_2(OAc)_4$, C_6H_6, 50°		202, 203
		$Rh_2(OAc)_4$, C_6H_6, 30°		219

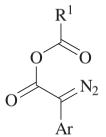
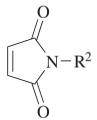
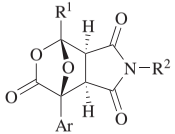
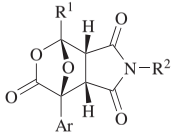
R^1	R^2	
Me	Me	(95)
Me	Et	(86)
4-ClC_6H_4	Me	(45)
4-ClC_6H_4	Et	(70)
4-$O_2NC_6H_4$	Me	(92)
4-$O_2NC_6H_4$	Et	(81)
4-$MeOC_6H_4$	Me	(92)
4-$MeOC_6H_4$	Et	(81)

I **II** **III**

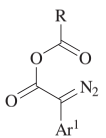
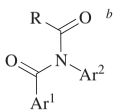
R	Ar	I/II/III	I[a]
Me	4-$O_2NC_6H_4$	55:28:17	(14)
4-ClC_6H_4	4-ClC_6H_4	60:27:13	(11)
4-ClC_6H_4	4-$O_2NC_6H_4$	55:24:21	(21)
4-$MeOC_6H_4$	4-$O_2NC_6H_4$	50:19:31	(24)

TABLE 12. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM ESTERS OR ANHYDRIDES (*Continued*)

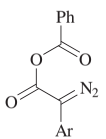
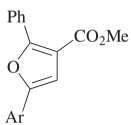
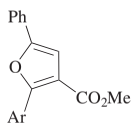
B. 1,3-DIOXOLIUMS (*Continued*)

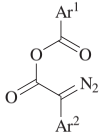
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-15}  $Ar = 4\text{-}O_2NC_6H_4$		$Pd(\pi\text{-allyl})$ complex, C_6H_6, 60–70°	 **I** +  **II**	218

R^1	R^2	**I**	**II**	**I/II**
Me	Me	(—)	(—)	5:1
Ph	Me	(61)	(—)	2:1
Ph	Ph	(—)	(—)	3:2

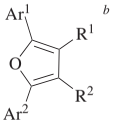
 $Ar^1 = 4\text{-}O_2NC_6H_4$		$Rh_2(OAc)_4$, C_6H_6, 50°	 [b]	203

R	Ar^2		
Me	Ph	(84)	
Me	4-NCC_6H_4	(95)	
4-ClC_6H_4	Ph	(81)	
4-ClC_6H_4	4-NCC_6H_4	(60)	
4-$MeOC_6H_4$	Ph	(84)	
4-$MeOC_6H_4$	4-NCC_6H_4	(95)	

C_{15}  $Ar = 4\text{-}O_2NC_6H_4$		$Pd(\pi\text{-allyl})$ complex, C_6H_6, 80°	 (49) +  (21)	217

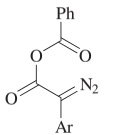


Pd(π-allyl) complex, C_6H_6, 80°

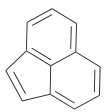

[b]

217

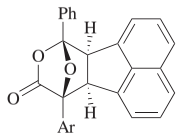
Ar^1	Ar^2	R^1	R^2	
Ph	4-$O_2NC_6H_4$	MeO_2C	MeO_2C	(86)
4-ClC_6H_4	4-ClC_6H_4	MeO_2C	MeO_2C	(74)
Ph	4-$O_2NC_6H_4$	H	*n*-Bu	(—)
Ph	4-$O_2NC_6H_4$	H	Ph	(—)
Ph	4-$O_2NC_6H_4$	Ph	MeO_2C	(—)
Ph	4-$O_2NC_6H_4$	Ph	Ph	(—)
Ph	4-$O_2NC_6H_4$	Bz	Bz	(—)



Ar = 4-$O_2NC_6H_4$

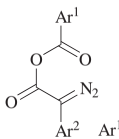


Pd(π-allyl) complex, C_6H_6, 60–70°



(71)

218

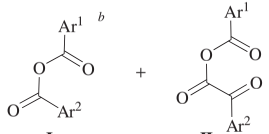


$^1O_2$

Ar^1 = 4-$MeOC_6H_4$

Ar^2 = 4-$O_2NC_6H_4$

$Rh_2(OAc)_4$, C_6H_6, 30°, 9,10-diphenylanthracene, tungsten lamp


[b]

I **II**

I + **II** (—), **I**/**II** = 4:5

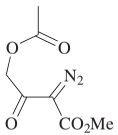
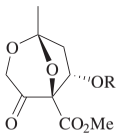
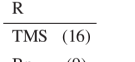
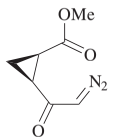
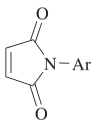
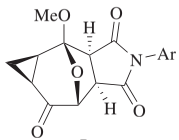
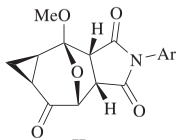
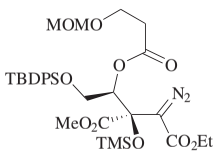
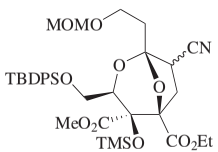
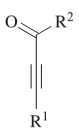
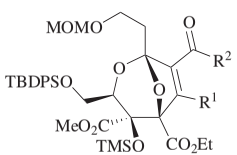
203

[a] This value is the yield after SiO_2 chromatography.

[b] The product results from loss of CO_2 from the intermediate cycloadduct.

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS

A. NON-AROMATIC YLIDES

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*				
C_6				
		$Rh_2(OAc)_4$, C_6H_6, 70°	 	151
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 + 	220
C_9				
		$Rh_2(OAc)_4$, C_6H_6, 80°		47, 165
		$Rh_2(OAc)_4$, C_6H_6, 80°		47, 165

I

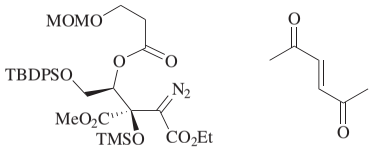
Ar	I	II
Ph	(25)	(16)
4-ClC_6H_4	(25)	(17)
4-MeC_6H_4	(31)	(16)

II

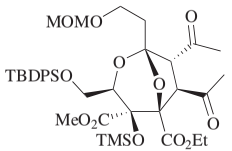
R	
TMS	(16)
Bn	(9)

α (31) + β (44)

R^1	R^2	
H	MeO	(82)
H	Me	(85)
MeO_2C	MeO	(66)

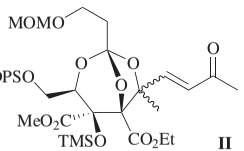


$Rh_2(OAc)_4$, C_6H_6, 80°



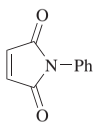
I

\+

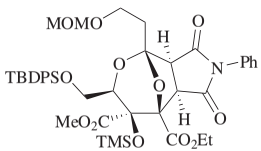


II

I	**II**	
(47)	(—)	165, 221
(47)	(31)	47



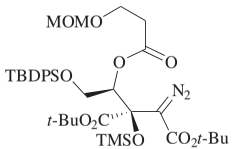
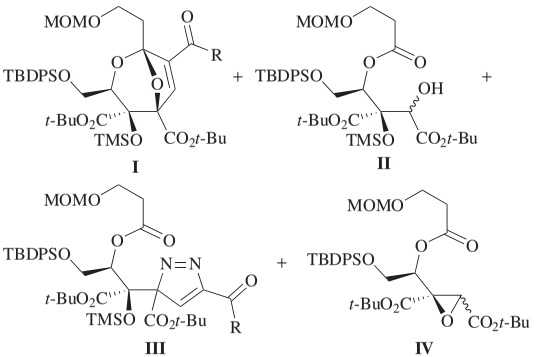
$Rh_2(OAc)_4$, C_6H_6, 80°



(68) 47

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

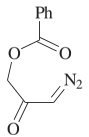
A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		Catalyst		

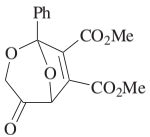
R	Catalyst	Solvent	Temp (°)	Time (min)	I	II	III	IV	Refs.
Me	$Rh_2(OAc)_4$	C_6H_6	80	—	(72)	(—)	(—)	(—)	165, 266
Me	$Rh_2(OAc)_4$	C_6H_6	80	40	(72)	(14)	(6)	(6)	47
Me	$Rh_2(OAc)_4$	C_6H_6	80	140	(67)	(10)	(3)	(7)	47
Me	$Rh_2(OAc)_4$	C_6H_6	80	150	(7)	(65)	(0)	(0)	47
Me	$Rh_2(OAc)_4$	toluene	80	40	(28)	(35)	(8)	(10)	47
Me	$Rh_2(OAc)_4$	toluene	110	25	(46)	(15)	(4)	(15)	47
Me	$Rh_2(OAc)_4$	DCE	80	20	(17)	(8)	(2)	(2)	47
Me	$Rh_2(OCOC_7H_{15})_4$	C_6H_6	80	40	(71)	(6)	(0)	(trace)	47
Me	$Rh_2(OCOPh)_4$	C_6H_6	80	40	(66)	(14)	(0)	(13)	47

Me	$Rh_2(pfb)_4$	C_6H_6	80	40	(11)	(4)	(0)	(33)	47
Me	$Rh_2(NHAc)_4$	C_6H_6	80	40	(72)	(3)	(0)	(trace)	47
MeO	$Rh_2(OAc)_4$	C_6H_6	80	40	(78)	(9)	(—)	(0)	47

C_{10}



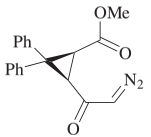
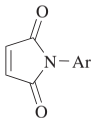
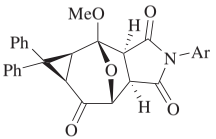
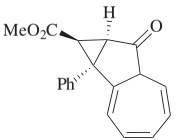
Catalyst **9c**, $PhCF_3$, rt



(10) er 57.0:43.0 98

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

A. NON-AROMATIC YLIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 		Catalyst, CH_2Cl_2, rt	 **I** +  **II**	220

Ar	Catalyst	I	II	III
Ph	$Rh_2(OAc)_4$	(41)	(28)	(3)
Ph	$Cu(acac)_2$	(15)	(45)	(3)
4-ClC_6H_4	$Rh_2(OAc)_4$	(41)	(29)	(3)
4-MeC_6H_4	$Rh_2(OAc)_4$	(44)	(26)	(3)

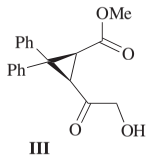
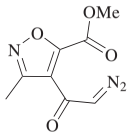
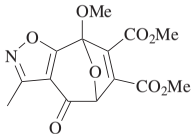
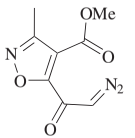
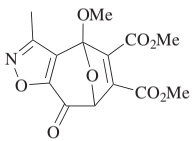
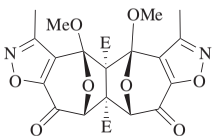
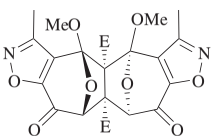
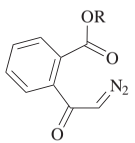
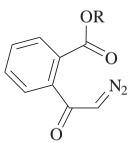
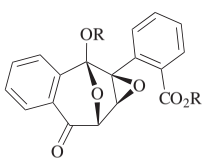
+  **III**

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS

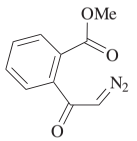
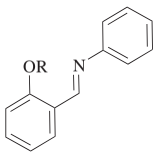
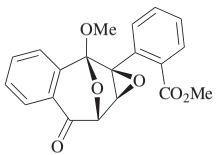
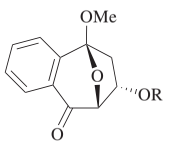
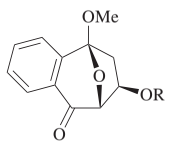
B. PYRYLIUMS

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*				
C_7				
		$Rh_2(OAc)_4$, toluene, 110°	 (68) + 2:1 adduct (2)	114
		$Rh_2(OAc)_4$, toluene, 110°	 +  **I** (59) **II**	114
			+  **II** + **III** (10) E = MeO_2C **III**	
C_9				
		Catalyst (*x* mol %), C_6H_6, 80°		317, 150, 259

R	Catalyst	*x*		
Me	$Cu(acac)_2$	—	(30)	317
Me	$Cu(acac)_2$	2	(27)	150, 259
Me	$Rh_2(OAc)_4$	0.4	(75)	259
i-Pr	$Rh_2(OAc)_4$	0.4	(62)	259

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

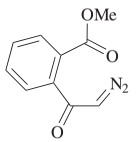
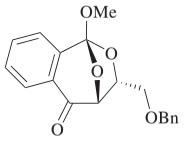
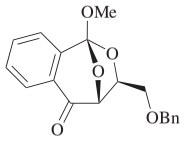
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Rh_2(OAc)_4$ (2 mol %), toluene, reflux	 R: Me (22); Bn (50)	44
		$Rh_2(OAc)_4$ (2 mol %), catalyst/M(OTf)$_3$ (10 mol %), 4 Å MS, CH_2Cl_2	 **I** +  **II**	

R	Catalyst	M	Temp	**I** + **II**	**I**/**II**	er **I**	er **II**	
TBS	**16c**	Eu	reflux[a,b]	(13)	100:0	58.5:41.5	—	104
Et	**16c**	Eu	reflux	(92)	83:17	91.5:8.5	—	103, 104
n-Bu	**16a**	Yb	rt	(44)	83:17	52.0:48.0	—	103
n-Bu	**16b**	Yb	rt	(48)	84:16	51.0:49.0	—	103
n-Bu	**16c**	Yb	rt	(57)	75:25	81.0:19.0	—	103

n-Bu	**16c**	Yb	reflux	(80)	75:25	83.5:16.5	70.0:30.0	103, 104
n-Bu	**16c**	Eu	reflux	(94)	81:19	90.5:9.5	78.0:22.0	103, 104
n-Bu	**16a**	Gd	reflux	(>99)	81:19	92.5:7.5	81.0:19.0	103, 104
n-Bu	**16b**	Ho	reflux	(89)	79:21	92.5:7.5	83.0:17.0	103, 104
n-Bu	**16c**	La	reflux	(87)	76:24	75.5:24.5	67.0:33.0	103, 104
n-Bu	**16c**	Sm	reflux	(74)	79:21	79.5:20.5	72.0:28.0	103, 104
n-Bu	**16c**	Tb	reflux	(65)	79:21	83.5:16.5	65.5:34.5	103, 104
n-Bu	**16c**	Er	reflux	(97)	79:21	92.0:8.0	85.5:14.5	103, 104
n-Bu	**16c**	Tm	reflux	(78)	77:23	90.5:9.5	76.0:24.0	103, 104
n-Bu	**16c**	Eu	0°	(20)	86:14	54.0:46.0	—	103
n-Bu	**16c**	Eu	rt	(48)	77:23	68.0:32.0	—	103
n-Bu	**16c**	Eu	30°	(78)	81:19	88.0:12.0	—	103
t-Bu	**16c**	Eu	reflux	(91)	87:13	94.0:6.0	—	103, 104
Cy	**16c**	Eu	reflux	(>99)	88:12	97.5:2.5	—	103, 104
Cy	**16c**	Gd	reflux	(93)	88:12	97.0:3.0	—	103, 104
Cy	**16c**	Ho	reflux	(99)	88:12	98.0:2.0	—	103, 104
Cy	**16c**	Eu	reflux[a]	(63)	89:11	84.5:15.5	—	104
Cy	**16c**	Eu	reflux[a,b]	(>99)	89:11	98.0:2.0	—	104
Cy	**16c**	Eu	reflux[a,b,c]	(99)	90:10	97.5:2.5	—	104
Bn	**16c**	Eu	reflux[a,b]	(61)	80:20	80.5:19.5	—	104
4-$MeOC_6H_4CH_2$	**16c**	Eu	reflux[a,b]	(64)	82:18	89.5:10.5	—	104

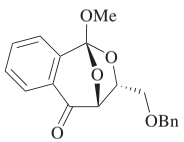
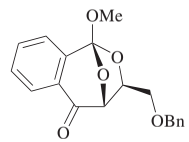
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Rh_2(OAc)_4$ (*x* mol %), additives, CH_2Cl_2, rt	 **I** +  **II**	192

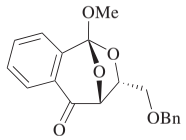
x	Additives	I + II	I/II	er I	er II
—	—	(96)	31:69	—	—
2	$Yb(OTf)_3$ (10 mol %), 4 Å MS	(97)	7:93	—	—
2	(*R*)-BINOL/$Yb(OTf)_3$ (10 mol %), TMP, 4 Å MS	(97)	9:91	51.0:49.0	50.0:50.0
2	(*S*)-BINOL/$Ti(O\textit{i}\text{-}Pr)_2Cl_2$ (10 mol %), 4 Å MS	(—)	32:68	51.5:48.5	51.5:48.5
2	Yb[(*S*)-BNP]$_3$ (10 mol %), 4 Å MS	(—)	43:57	76.0:24.0	57.0:43.0

1. Ligand/$M(OTf)_3$ (10 mol %), 4 Å MS, rt
2. $Rh_2(OAc)_4$ (2 mol %), CH_2Cl_2, −10°

 **I** +  **II**

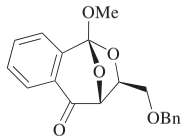
Ligand	M	Time (h)	I + II	I/II	er I	er II	
16a	Yb	2	(98)	9:91	32.5:67.5	32.0:68.0	100, 101
16a	Sc	2	(96)	88:12	4.5:95.5	41.0:59.0	100, 101
16a	Sc	2	(93)[d]	85:15	6.5:93.5	42.5:57.5	100, 101
16b	Yb	2	(100)	14:86	31.0:69.0	46.5:53.5	100, 101
16b	Sc	2	(57)	86:14	4.0:96.0	43.0:57.0	100, 101
17b	Sc	2	(50)	57:43	88.5:11.5	54.5:45.5	101

1. Ligand/M(OTf)$_3$ (10 mol %), temp, time
2. $Rh_2(OAc)_4$ (2 mol %), CH_2Cl_2, −10°



I

+

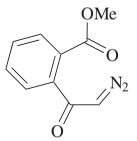
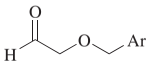
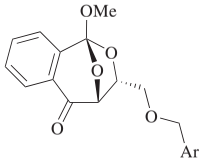
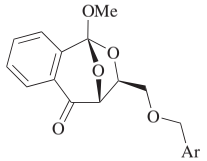


II

Ligand	M	Temp	Time (h)	**I** + **II**	**I**/**II**	er **I**	er **II**	
17a	Sc	rt	2	(81)	5:95	66.0:34.0	55.0:45.0	101
16a	Yb	rt	2	(99)	9:91	30.0:70.0	30.0:70.0	100, 101
16a	Sc	rt	1	(85)	5:95	50.5:49.5	50.0:50.0	101
16a	Sc	rt	2	(91)	55:45	7.5:92.5	42.0:58.0	100, 101
16a	Sc	rt	6	(94)	76:24	7.0:93.0	33.0:67.0	100, 101
16a	Sc	reflux	2	(87)	77:23	6.0:94.0	42.0:58.0	100, 101
17b	Yb	rt	2	(86)	6:94	54.0:46.0	55.5:44.5	101
17b	Sc	rt	2	(98)	29:71	87.5:12.5	59.0:41.0	100, 101

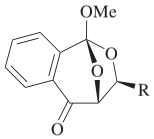
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Rh_2(OAc)_4$ (2 mol %), ligand **16a**/$Sc(OTf)_3$ (10 mol %), 4 Å MS, CH_2Cl_2	 +  **I** **II**	100, 101

Ar	Temp (°)	I + II	I/II	er I	er II
Ph	−10	(96)	88:12	95.5:4.5	59.0:41.0
4-FC_6H_4	−10	(97)	82:18	96.5:3.5	61.0:39.0
4-ClC_6H_4	−25	(84)	73:27	93.0:7.0	55.0:45.0
4-BrC_6H_4	−25	(77)	67:33	91.5:8.5	52.5:47.5
2-$MeOC_6H_4$	−10	(82)	85:15	91.0:9.0	57.5:42.5
4-$MeOC_6H_4$	−10	(53)	91:9	94.5:5.5	56.0:44.0

Catalyst, additive,
solvent



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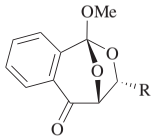
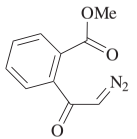
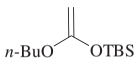
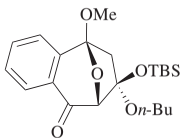
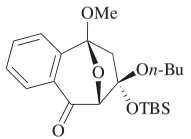


I **II**

R	Catalyst	Additive(s)	Solvent	Temp	Time (h)	**I**	**II**	
Me	$Cu(acac)_2$	—	C_6H_6	80°	~1	(25)	(39)	318
Et	$Cu(acac)_2$	—	C_6H_6	80°	~1	(21)	(23)	318, 319
n-Pr	$Rh_2(OAc)_4$ (2 mol %)	4 Å MS pwd.	CH_2Cl_2	rt	1	(41)	(41)	192
n-Pr	$Rh_2(OAc)_4$ (2 mol %)	$Yb(OTf)_3$ (10 mol %), 4 Å MS pwd.	CH_2Cl_2	rt	1	(40)	(60)	192
i-Pr	$Cu(acac)_2$	—	C_6H_6	80°	~1	(47)	(30)	318
i-Pr	$Rh_2(OAc)_4$ (2 mol %)	4 Å MS pwd.	CH_2Cl_2	rt	1	(54)	(23)	192
i-Pr	$Rh_2(OAc)_4$ (2 mol %)	$Yb(OTf)_3$ (10 mol %), 4 Å MS pwd.	CH_2Cl_2	rt	1	(22)	(43)	192
i-Pr	$Rh_2(OAc)_4$ (2 mol %)	$Yb(OTf)_3$ (10 mol %), 4 Å MS pwd.	Et_2O	rt	1	(20)	(17)	192
t-Bu	$Cu(acac)_2$	—	C_6H_6	80°	~1	(57)	(11)	318
Cy	$Rh_2(OAc)_4$ (2 mol %)	4 Å MS pwd.	CH_2Cl_2	rt	1	(59)	(24)	192
Cy	$Rh_2(OAc)_4$ (2 mol %)	$Yb(OTf)_3$ (10 mol %), 4 Å MS pwd.	CH_2Cl_2	rt	1	(66)	(29)	192

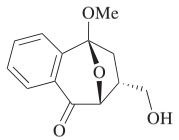
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Rh_2(OAc)_4$ (2 mol %), ligand/M(OTf)$_3$ (10 mol %, 5×10^{-3} M), 4 Å MS	 **I** +  **II**	104

Ligand	M	Solvent	Temp (°)	I + II	I/II	er I	er II
16c	Eu	CH_2Cl_2[a,b]	reflux	(54)	28:72	76.5:23.5	63.5:36.5
16c	Lu	CH_2Cl_2[a,b]	reflux	(41)	42:58	78.0:22.0	63.0:37.0
16c	Lu	$CHCl_3$	45	(36)	46:54	83.5:16.5	71.0:29.0
16b	Lu	$CHCl_3$	45	(29)	64:36	79.0:21.0	72.0:28.0
16a	Lu	$CHCl_3$	45	(24)	76:24	82.5:17.5	78.0:22.0
16a	Lu	toluene	45	(68)	74:26	86.0:14.0	77.5:22.5
16a	Lu	toluene[e]	45	(63)	74:26	85.0:15.0	86.5:13.5
16a	Lu	toluene[f]	45	(49)	72:28	85.0:15.0	86.0:14.0

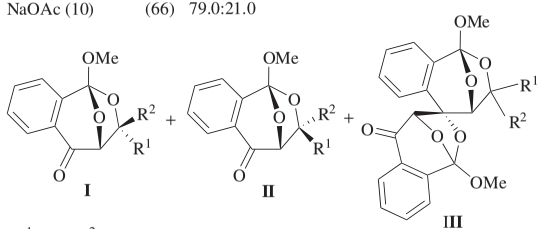
$Rh_2(OAc)_4$ (2 mol %), ligand **16c**/$M(OTf)_3$ (10 mol %), 4 Å MS, reflux



104

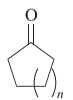
M	Solvent	Additive (mol %)		er
Eu	CH_2Cl_2[a]	MeOH (10)	(32)	72.5:27.5
Eu	$CHCl_3$	—	(59)	75.5:24.5
Ho	$CHCl_3$	—	(70)	77.5:22.5
Ho	$CHCl_3$	K_2CO_3 (30)	(61)	80.0:20.0
Ho	$CHCl_3$	LiF (30)	(73)	79.5:20.5
Ho	$CHCl_3$	NaOAc (10)	(66)	79.0:21.0

$Cu(acac)_2$, C_6H_6, 80°

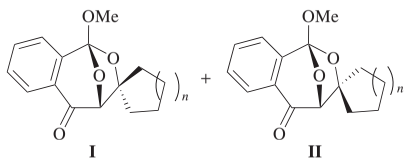


I **II** **III**

R^1	R^2	**I**	**II**	**III**	**I** + **II**	
Me	Me	(—)	(—)	(12)	(75)	318, 320
Me	Et	(38)	(20)	(—)	(—)	320
Me	*i*-Pr	(35)	(15)	(—)	(—)	320
$ClCH_2$	$ClCH_2$	(—)	(—)	(—)	(96)	320



$Cu(acac)_2$, C_6H_6, 80°

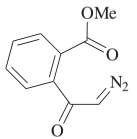
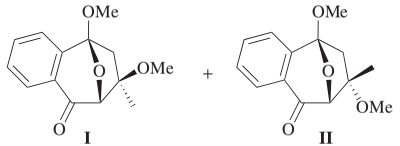
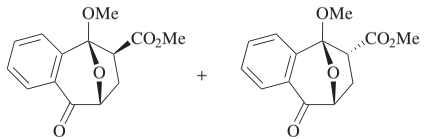


I **II**

n	**I** + **II**	
1	(78)	320
2	(87)	

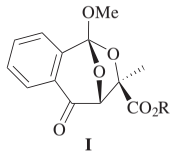
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Rh_2(OAc)_4$ (2 mol %), ligand **16c**/Eu(OTf)$_3$ (10 mol %), 4 Å MS, CH_2Cl_2, reflux	 **I** + **II** (23), **I/II** = 53:47; er **I** 56.0:44.0, er **II** 57.5:42.5	104
		$Rh_2(OAc)_4$ (2 mol %), M(OTf)$_3$ (*x* mol %), 4 Å MS		140

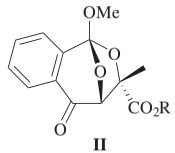
M	*x*	Solvent	Temp	**I** + **II**	**I/II**
—	—	CH_2Cl_2	rt	(92)	29:71
Sc	(10)	CH_2Cl_2	rt	(82)	21:79
Yb	(10)	CH_2Cl_2	rt	(87)	21:79
Yb	(50)	CH_2Cl_2	rt	(65)	15:85
Yb	(50)	CH_2Cl_2	0°	(70)	29:71
Yb	(10)	toluene	rt	(81)	33:67
Yb	(10)	Et_2O	rt	(74)	24:76
Eu	(10)	CH_2Cl_2	rt	(89)	20:80
La	(10)	CH_2Cl_2	rt	(88)	26:74

1. Ligand/Sc(OTf)$_3$ (10 mol %), $Rh_2(OAc)_4$ (2 mol %), 4 Å MS, CH_2Cl_2, −10°
2. Additive
3. Dipolarophile



I

+



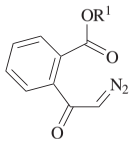
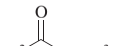
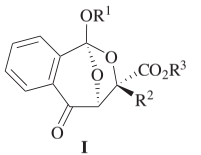
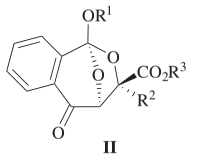
II

101

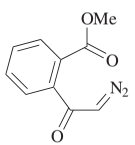
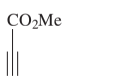
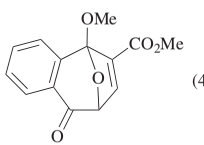
R	Ligand	Additive (mol %)	**I** + **II**	**I**/**II**	er **I**	er **II**
Me	**17b**	—	(95)	96:4	76.5:23.5	65.0:35.0
Me	**17c**	—	(93)	92:8	74.5:25.5	68.0:32.0
Me	**17d**	—	(93)	95:5	78.0:22.0	72.0:28.0
Me	**16a**	—	(84)	88:12	27.0:73.0	37.0:63.0
Me	**16a**	$MeCOCO_2H$ (10)	(88)	96:4	11.0:89.0	20.0:80.0
Me	**16a**	$MeCOCO_2H$ (20)	(71)	94:6	14.5:85.5	—
Me	**16a**	CF_3CO_2H (10)	(97)	96:4	8.0:92.0	15.5:84.5
Bn	**16a**	—	(82)	82:18	44.5:55.5	49.0:51.0
Bn	**16a**	MeCOMe (20)	(84)	83:17	36.0:64.0	39.0:61.0
Bn	**16a**	$MeCO_2H$ (20)	(90)	87:13	27.0:73.0	42.0:58.0
Bn	**16a**	$MeCOCH_2CH_2CO_2H$ (20)	(86)	86:14	25.5:74.5	39.5:60.5
Bn	**16a**	$CH_2(CO_2H)_2$ (20)	(85)	84:16	36.0:64.0	45.0:55.0
Bn	**16a**	$CH_2(COCH_3)_2$ (20)	(64)	76:24	48.5:51.5	52.0:48.0
Bn	**16a**	$MeCOCO_2H$ (10)	(94)	93:7	9.0:91.0	13.0:87.0
Bn	**16a**	$MeCOCO_2H$ (20)	(88)	93:7	6.5:93.5	16.5:83.5
Bn	**16a**	TfOH (10)	(73)	81:19	34.5:65.5	25.5:74.5
Bn	**16a**	TfOH (20)	(75)	81:19	32.0:68.0	22.5:77.5
Bn	**16a**	CF_3CO_2H (10)	(100)	94:6	5.0:95.0	6.0:94.0
Bn	**16a**[d]	CF_3CO_2H (10)	(98)	93:7	3.0:97.0	2.5:97.5
Bn	**16a**[g]	CF_3CO_2H (10)	(100)	92:8	8.0:92.0	16.5:83.5
Bn	**16a**[h]	CF_3CO_2H (10)	(98)	92:8	9.5:90.5	18.0:82.0
Bn	**16a**	CF_3CO_2H (20)	(100)	92:8	9.0:91.0	21.5:78.5

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

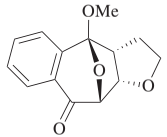
B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		Ligand **16a**/$Sc(OTf)_3$ (10 mol %), 4 Å MS, CF_3CO_2H, $Rh_2(OAc)_4$ (2 mol %), CH_2Cl_2, −10°	 **I** +  **II**	101

R^1	R^2	R^3	**I** + **II**	**I**/**II**	er **I**	er **II**
Me	H	Bn	(77)	89:11	63.5:36.5	53.0:47.0
Me	Me	Me	(97)	96:4	92.0:8.0	84.5:15.5
Me	Me	4-FC_6H_4	(93)	96:4	97.0:3.0	97.5:2.5
Me	Me	4-ClC_6H_4	(95)	97:3	96.0:4.0	93.5:6.5
Me	Me	4-BrC_6H_4	(93)	96:4	96.5:3.5	94.0:6.0
Me	Me	4-$MeOC_6H_4$	(100)	96:4	97.0:3.0	97.0:3.0
Me	Me	Bn	(98)	93:7	97.0:3.0	97.5:2.5
Me	Et	Bn	(98)	93:7	94.5:5.5	80.5:19.5
Me	*i*-Pr	Bn	(100)	93:7	97.5:2.5	97.5:2.5
Me	*i*-Pr	4-BrC_6H_4	(98)	96:4	97.5:2.5	99.0:1.0
Me	EtO_2C	Et	(100)	—	72.5:27.5	—
Me	Ph	Me	(88)	68:32	90.0:10.0	72.5:27.5
Me	Ph	Bn	(95)	78:22	94.5:5.5	54.0:46.0
i-Pr	Me	Bn	(77)	88:12	96.5:3.5	99.0:1.0

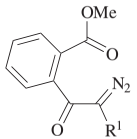
		$Cu(acac)_2$, C_6H_6, 80°	 (44)	185

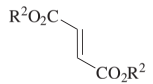
$Rh_2(OAc)_4$ (2 mol %), ligand **16c**/$M(OTf)_3$ (10 mol %), 4 Å MS



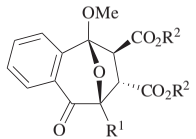
endo/*exo* = > 99:1

M	Solvent	Temp		er	
Eu	CH_2Cl_2	reflux	(98)	79.5:20.5	103, 104
Eu	toluene	45°	(96)	83.0:17.0	104
Yb	toluene	45°	(86)	83.5:16.5	104





Catalyst, additive, solvent



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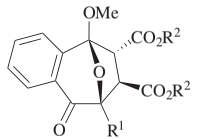
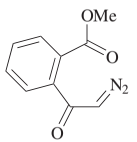
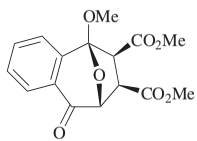


I **II**

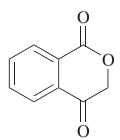
R^1	R^2	Catalyst (mol %)	Additive(s) (mol %)	Solvent	Temp	**I**	er **I**	**II**	er **II**	
H	Me	$Cu(acac)_2$	—	C_6H_6	80°	(—)	—	(70)	—	150
H	Me	$Cu(acac)_2$	—	C_6H_6	80°	(4)	—	(70)	—	321
H	Me	$Rh_2(OAc)_4$ (5)	—	C_6H_6	reflux	(17)	—	(72)	—	56
H	Me	$Rh_2(OAc)_4$ (2)	—	CH_2Cl_2	rt	(9)	—	(69)	—	56
H	Me	$Rh_2(OAc)_4$ (5)	$Yb(OTf)_3$ (5)	C_6H_6	reflux	(7)	—	(31)	—	56
H	Me	$Rh_2(OAc)_4$ (2)	$Yb(OTf)_3$ (10)	CH_2Cl_2	rt	(4)	—	(30)	—	56
H	Me	$Rh_2(OAc)_4$ (2)	$Yb(OTf)_3$ (10), 4 Å MS	CH_2Cl_2	rt	(3)	—	(69)	—	56
H	Me	**8d**	—	$PhCF_3$	rt	(31)	88.5:11.5	(29)	52.0:48.0	98
H	Et	$Cu(acac)_2$	—	C_6H_6	80°	(—)	—	(59)	—	150
D	Me	$Cu(acac)_2$	—	C_6H_6	80°	(—)	—	(60)	—	321



$Cu(acac)_2$, C_6H_6, 80°



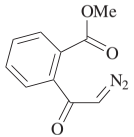
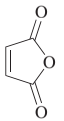
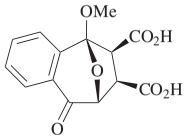
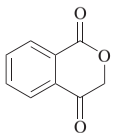
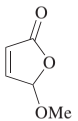
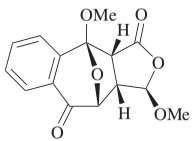
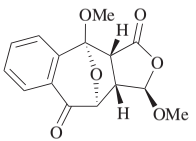
(51) +



(18) 321

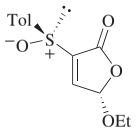
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

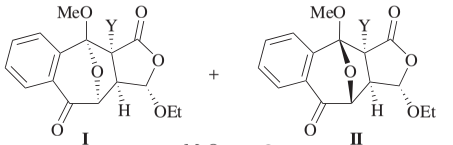
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Cu(acac)_2$, C_6H_6, 80°	 (48) +  (14)	321
		Catalyst, THF	 + 	93

I **II**

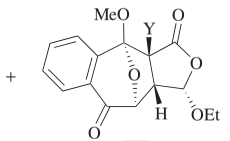
Catalyst	Temp	**I** + **II**	**I**/**II**
$Rh_2(OAc)_4$	rt	(17)	3:2
CuCl	—	(—)	3:2



$Rh_2(OAc)_4$

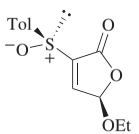


93

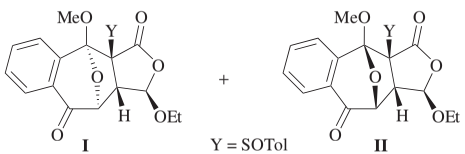


Y = SOTol

Diazo/Dipolarophile	Solvent	Temp	I	II	III	I/II/III
1:1	THF	rt	(—)	(—)	(—)	—
1:3	THF	rt	(23)	(20)	(21)	41:27:32
1:3	THF	0°	(—)	(—)	(—)	61:20:19
1:3	CH_2Cl_2	rt	(—)	(—)	(—)	54:28:18
1:3	MeCN	rt	(—)	(—)	(—)	58:18:24
1:3	MeCN	0°	(—)	(—)	(—)	62:17:21



$Rh_2(OAc)_4$



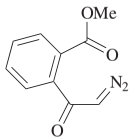
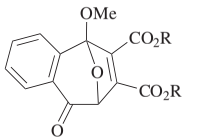
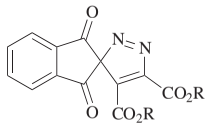
93

Y = SOTol

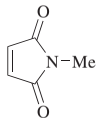
Solvent	Temp	I	II	I/II
THF	rt	(51)	(23)	76:24
THF	0°	(—)	(—)	81:19
CH_2Cl_2	rt	(—)	(—)	68:32
MeCN	rt	(—)	(—)	69:31

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

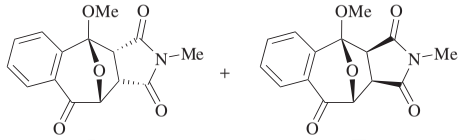
B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		Catalyst	 +  **I** **II**	

R	Catalyst	Solvent	Temp	**I**	er **I**	**II**	
Me	$Cu(acac)_2$	C_6H_6	80°	(73)	—	(4)	185
Me	$Cu(acac)_2$	C_6H_6	80°	(70)	—	(—)	150
Me	**8a**	$PhCF_3$	rt	(67)	72.0:28.0	(—)	98
Me	**8b**	$PhCF_3$	rt	(69)	67.5:32.5	(—)	98
Me	**8c**	$PhCF_3$	rt	(67)	75.5:24.5	(—)	98
Me	**8d**	$PhCF_3$	rt	(67)	87.0:13.0	(—)	98
Me	**9a**	$PhCF_3$	rt	(63)	76.0:24.0	(—)	98
Me	**9b**	$PhCF_3$	rt	(68)	67.0:33.0	(—)	98
Me	**9c**	$PhCF_3$	rt	(72)	81.0:19.0	(—)	98
Me	**9d**	$PhCF_3$	rt	(68)	86.0:14.0	(—)	98
Me	**1a**	$PhCF_3$	rt	(84)	—	(—)	171
Et	**8d**	$PhCF_3$	rt	(47)	73.0:27.0	(—)	98
t-Bu	**8d**	$PhCF_3$	rt	(22)	62.5:37.5	(—)	98



Catalyst

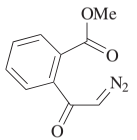
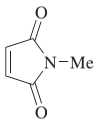
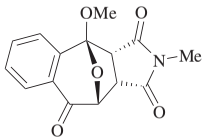
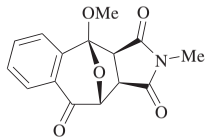


I **II**

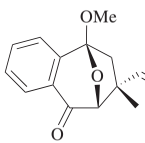
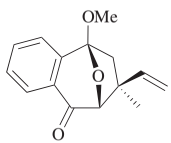
Catalyst (mol %)	Solvent	Temp	**I + II**	**I/II**	er **I**	er **II**	
CuOTf (5)	C_6H_6	reflux	(49)	87:13	—	—	56, 322
CuOTf (20)	C_6H_6	reflux	(34)	94:6	—	—	56, 322
$[Cu(MeCN)_4]PF_6$ (5)	C_6H_6	reflux	(49)	65:35	—	—	56
CuCl (5)	C_6H_6	reflux	(81)	26:74	—	—	56, 322
CuCl (5), $ZnBr_2$ (5)	C_6H_6	reflux	(27)	82:18	—	—	56
CuCl (5), $Yb(OTf)_3$ (5)	C_6H_6	reflux	(52)	94:6	—	—	56, 322
$Cu(OTf)_2$ (5)	C_6H_6	reflux	(24)	82:18	—	—	56, 322
$Cu(acac)_2$ (5)	C_6H_6	reflux	(66)	24:76	—	—	56
$Cu(acac)_2$ (5)	C_6H_6	80°	(94)	35:65	—	—	321, 323
$Cu(acac)_2$ (5), $Yb(OTf)_3$ (5)	C_6H_6	reflux	(46)	83:17	—	—	56
$Cu(hfacac)_2$ (5)	C_6H_6	reflux	(40)	32:68	—	—	56
$Rh_2(OAc)_4$ (5)	C_6H_6	reflux	(70)	11:89	—	—	56, 322
$Rh_2(OAc)_4$ (5), $Yb(OTf)_3$ (5)	C_6H_6	reflux	(64)	61:39	—	—	56
$Rh_2(OAc)_4$ (5), $Yb(OTf)_3$ (5)	C_6H_6	rt	(89)	90:10	—	—	56
$Rh_2(OAc)_4$ (1), $Yb(OTf)_3$ (5)	C_6H_6	rt	(69)	88:12	—	—	56
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)	C_6H_6	rt	(98)	93:3	—	—	56
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)	CH_2Cl_2	rt	(>99)	95:5	—	—	56
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)	CH_2Cl_2	0°	(95)	95:5	—	—	56
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)	THF	rt	(35)	99:1	—	—	56
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)	Et_2O	rt	(67)	99:1	—	—	56

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

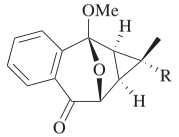
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9  (*Continued*)		Catalyst	 **I** +  **II**	

Catalyst (mol %)	Solvent	Temp	I + II	I/II	er I	er II	Refs.
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)[i]	Et_2O	rt	(89)	96:4	—	—	56
$Rh_2(tfa)_4$ (5)	C_6H_6	reflux	(40)	22:78	—	—	56
$Rh_2(acm)_4$ (5)	C_6H_6	reflux	(84)	35:65	—	—	56
$Yb(OTf)_3$ (10)[i]	C_6H_6	reflux[j]	(36)	98:2	—	—	56
$Sc(OTf)_3$ (10)[i]	C_6H_6	reflux[k]	(60)	77:23	—	—	56
15•CuOTf (5)	C_6H_6	reflux	(81)	29:71	50.5:49.5	50.0:50.0	56, 322
15•CuOTf (5)	C_6H_6	rt	(69)	50:50	51.5:48.5	50.0:50.0	56
15•$Cu(OTf)_2$ (5)	C_6H_6	reflux	(79)	49:51	50.5:49.5	50.0:50.0	56
15•$Cu(OTf)_2$ (5)	C_6H_6	rt	(60)	46:54	53.5:46.5	50.0:50.0	56
15•$[Cu(MeCN)_4]PF_6$ (5)	C_6H_6	reflux	(38)	47:53	53.0:47.0	50.0:50.0	56
(*S*)-**6**	C_6H_6	rt	(75)	23:77	50.0:50.0	51.0:49.0	56

		$Cu(acac)_2$, C_6H_6, 80°	 (43) +  (34)				150, 317

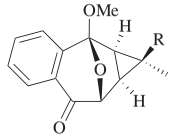
x eq

$Rh_2(OAc)_4$, CH_2Cl_2, rt



I

+



II

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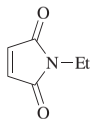
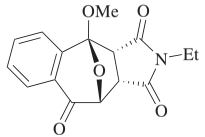
R	*x*	**I**	**II**
Me	3	(69)	(—)
Me	5	(85)	(—)
MeO_2C	3	(16)	(—)
Ph	3	(44)	(4)



Catalyst



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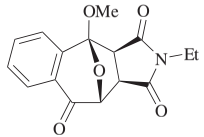
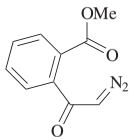
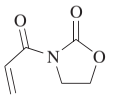
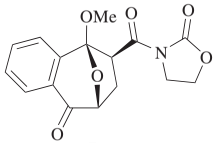
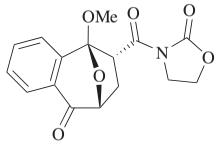


II

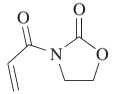
Catalyst (mol %)	Solvent	Temp	**I** + **II**	**I**/**II**	er **I**	er **II**	
$Cu(acac)_2$ (5)	C_6H_6	80°	(95)	26:74	—	—	321
CuOTf (5)	C_6H_6	rt	(44)	82:18	—	—	56, 322
CuOTf (5)	C_6H_6	reflux	(55)	70:30	—	—	56
$[Cu(MeCN)_4]PF_6$ (5)	C_6H_6	reflux	(47)	69:31	—	—	56
CuCl (5), $Yb(OTf)_3$ (5)	C_6H_6	reflux	(40)	88:12	—	—	56, 322
$Rh_2(OAc)_4$ (5)	C_6H_6	reflux	(85)	22:78	—	—	56, 322
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)	CH_2Cl_2	rt	(76)	95:5	—	—	56
$Rh_2(OAc)_4$ (2), $Yb(OTf)_3$ (10)[i]	CH_2Cl_2	rt	(80)	90:10	—	—	56
15•CuOTf (5)	C_6H_6	rt	(51)	33:67	53.5:46.5	50.0:50.0	56

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

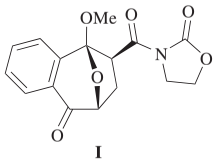
B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Rh_2(OAc)_4$ (2 mol %), additive, 4 Å MS, CH_2Cl_2	 **I** +  **II**	

Additive (mol %)	Temp	I + II	I/II	Refs.
—	rt[l]	(82)	20:80	102, 140
$Sc(OTf)_3$ (10)	rt	(86)	60:40	140
$Lu(OTf)_3$ (10)	rt	(84)	83:17	140
$Yb(OTf)_3$ (20)	rt	(88)	84:16	140
$Yb(OTf)_3$ (50)	rt	(93)	87:13	140
$Yb(OTf)_3$(100)	rt	(79)	86:14	140
$Yb(OTf)_3$ (10)	rt[l]	(88)	81:19	102, 140
$Yb(OTf)_3$ (10)	reflux	(91)	78:22	140
$Yb(OTf)_3$ (10)	−10°	(80)	40:60	140
$Tm(OTf)_3$ (10)	rt	(93)	79:21	140
$Er(OTf)_3$ (10)	rt	(93)	78:22	140
$Ho(OTf)_3$ (10)	rt	(88)	74:26	140
$Eu(OTf)_3$ (10)	rt	(88)	43:57	140
$Sm(OTf)_3$ (10)	rt	(91)	48:52	140
$La(OTf)_3$ (10)	rt	(84)	49:51	140
$Mg(OTf)_2$ (10)	rt	(89)	20:80	140



$Rh_2(OAc)_4$ (2 mol %),
ligand/additive(s)
CH_2Cl_2



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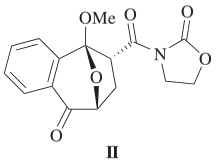
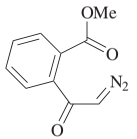
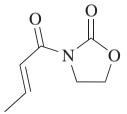
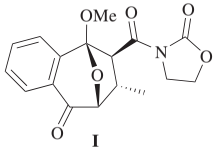
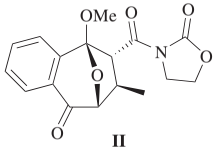


II

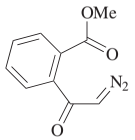
Ligand/Additive(s) (mol %)	Temp (°)	Time (h)	**I** + **II**	**I**/**II**	er **I**	er **II**	
—	−25	1	(90)	19:81	—	—	140
terpyridine/Yb(OTf)$_3$ (10), 4 Å MS	−10	1	(82)	40:60	—	—	140
terpyridine/Lu(OTf)$_3$ (10), 4 Å MS	−10	1	(89)	43:57	—	—	140
16a/Sc(OTf) (10), 4 Å MS	−10	1	(65)	10:90	50.5:49.5	54.0:46.0	100, 140
16a/Yb(OTf) (10), 4 Å MS	−10	1	(90)	12:88	61.0:39.0	56.5:43.5	100, 140
16b/Yb(OTf)^m (10), H_2O, 4 Å MS	−10	1	(88)	52:48	60.5:39.5	50.5:49.5	101
16b/Yb(OTf)^n (10), H_2O, 4 Å MS	−10	1	(88)	61:39	76.0:24.0	51.5:48.5	101
16b/Yb(OTf)^o (10), H_2O (30)	−10	1	(43)	33:67	84.5:15.5	52.5:47.5	101
16b/Yb(OTf)^p (10), H_2O (20), 4 Å MS	−10	1	(76)	73:27	95.5:4.5	54.0:46.0	101
16b/Yb(OTf)^p (10), H_2O (10), 4 Å MS	−10	1	(98)	90:10	96.0:4.0	54.0:46.0	101
16b/Yb(OTf)^p (10), H_2O (10), 4 Å MS	−10	1	(51–94)^r	67:33–83:17	95.0:5.0–99.0:1.0	51.0:49.0–55.0:45.0	101
16b/Yb(OTf)^q (10), H_2O (10), 4 Å MS	−10	1	(72)	74:26	97.5:2.5	52.5:47.5	101
16b/Yb(OTf)^q (10), H_2O (10), 4 Å MS	−10	1	(59–93)^r	73:27–77:23	92.0:8.0–97.5:2.5	52.5:47.5–55.0:45.0	101
16b/Yb(OTf) (10), 4 Å MS	−10	1	(94)	54:46	94.5:5.5	—	100, 140
16b/Yb(OTf) (10), 4 Å MS	−10	3	(97)	70:30	95.5:4.5	—	100, 140
16b/Yb(OTf) (10), 4 Å MS	−10	6	(94)	82:18	98.0:2.0	54.0:46.0	102
16b/Yb(OTf) (10), 4 Å MS	−10	6	(89)	88:12	99.0:1.0	—	100, 140
16b/Sc(OTf) (10), 4 Å MS	−25	1	(86)	11:89	57.0:43.0	53.5:46.5	100, 140
17b/Sc(OTf)$_3$ (10), 4 Å MS	−10	1	(92)	15:85	—	—	100, 140
17b/Yb(OTf)$_3$ (10), 4 Å MS	−10	1	(91)	23:77	—	—	100, 140

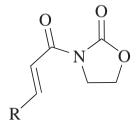
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

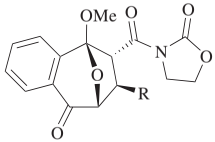
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9  Addition time = *x* h		$Rh_2(OAc)_4$ (2 mol %), $M(OTf)_3$ (10 mol %), 4 Å MS, CH_2Cl_2	 **I** +  **II**	102

M	*x*	**I** + **II**	**I**/**II**
—	1	(71)	17:83
Sc	1	(33)	15:85
Yb	1	(55)	40:60
Yb	6	(58)	52:48
Tm	6	(70)	63:37
Er	6	(84)	61:39
Ho	6	(75)	54:46
Eu	6	(78)	38:62
La	6	(41)	30:70





$Rh_2(OAc)_4$ (2 mol %),
ligand/$M(OTf)_3$
(*x* mol %), 4 Å MS,
CH_2Cl_2



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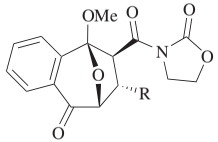


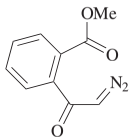
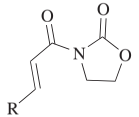
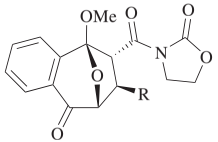
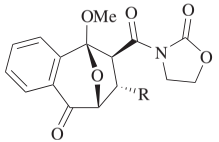
II

102

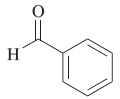
R	Ligand	M	*x*	Temp	**I** + **II**	**I**/**II**	er **I**	er **II**
Me	**16b**	Yb	10	reflux	(65)	97:3	65.0:35.0	76.0:24.0
Me	**16b**	Yb	10	rt	(71)	99:1	64.0:36.0	60.0:40.0
Me	**16b**	Yb	10	−10°	(18)	97:3	69.0:31.0	76.0:24.0
Me	**16b**	Yb	10	−25°	(5)	97:3	65.0:35.0	76.0:24.0
Me	**16b**	Tm	10	rt	(81–68)[r]	95:5–93:7	87.0:13.0–63.0:37.0	55.0:45.0–52.0:48.0
Me	**16b**	Er	10	rt	(53)	96:4	59.0:41.0	60.0:40.0
Me	**16b**	Ho	10	rt	(50)	95:5	61.0:39.0	60.0:40.0
Me	**16b**	Eu	10	rt	(88)	97:3	46.0:54.0	69.0:31.0
Me	**16b**	La	10	rt	(34)	90:10	38.0:62.0	68.0:32.0
Me	**16c**	Yb	10	reflux	(79)	97:3	75.0:25.0	>99.5:0.5
Me	**16c**	Yb	10	rt	(67)	92:8	70.0:30.0	58.0:42.0
Me	**16c**	Yb	10	−10°	(8)	94:6	72.0:28.0	71.0:29.0
Me	**16c**	Tm	10	rt	(50)	96:4	70.0:30.0	>99.5:0.5
Me	**16c**	Er	10	rt	(59)	97:3	71.0:29.0	88.0:12.0
Me	**16c**	Ho	10	rt	(57)	96:4	76.0:24.0	95.0:5.0
Me	**16c**	Eu	10	rt	(96)	98:2	62.0:38.0	75.0:25.0
Me	**16c**	La	10	rt	(83)	90:10	54.0:46.0	58.0:42.0
Et	**16c**	Yb	10	rt	(32)	>99:1	65.0:35.0	—
Et	**16c**	Yb	20	rt	(47)	99:1	64.0:36.0	—
Et	**16c**	Yb	30	rt	(49)	98:2	69.0:31.0	—

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

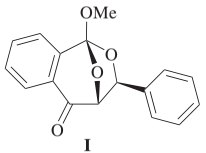
B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9  (*Continued*)		$Rh_2(OAc)_4$ (2 mol %), ligand/M(OTf)$_3$ (*x* mol %), 4 Å MS, CH_2Cl_2	 **I** +  **II**	102

R	Ligand	M	*x*	Temp	**I** + **II**	**I**/**II**	er **I**	er **II**
EtO_2C	**16c**	Yb	10	rt	(54)	76:24	89.0:11.0	—
EtO_2C	**16c**	Yb	20	rt	(51)	83:17	89.0:11.0	—
EtO_2C	**16c**	Yb	30	rt	(55)	93:7	84.0:16.0	—
Ph	**16b**	Yb	10	reflux	(13)	>99:1	86.0:14.0	—



$Rh_2(OAc)_4$ (2 mol %),
additive(s), 1 h



I

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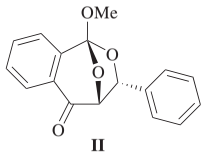
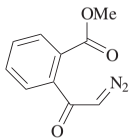
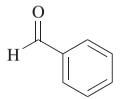
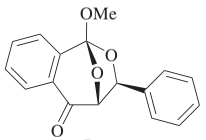
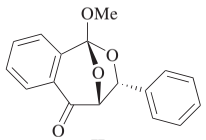


II

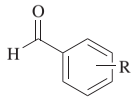
Additive(s) (mol %)	Solvent	Temp	**I** + **II**	**I**/**II**	er **I**	er **II**	
—	CH_2Cl_2	rt	(77)	51:49	—	—	192
4 Å MS pwd.	CH_2Cl_2	rt	(83)	50:50	—	—	192
ATPH	CH_2Cl_2	rt	(68)	51:49	—	—	192
MAD	CH_2Cl_2	rt	(76)	54:46	—	—	192
$Yb(OTf)_3$ (10)	CH_2Cl_2	rt	(76)	94:6	—	—	192
$Yb(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(96)	90:10	—	—	192
Yb(OTf) (10), 4 Å MS 1/16	CH_2Cl_2	rt	(86)	92:8	—	—	192
Yb(OTf) (10), 3 Å MS pwd.	CH_2Cl_2	rt	(83)	88:12	—	—	192
Yb(OTf) (10), 5 Å MS pwd.	CH_2Cl_2	rt	(80)	93:7	—	—	192
$Mg(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(93)	51:49	—	—	192
$Sc(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(82)	69:31	—	—	192
$Lu(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(100)	89:11	—	—	192
$Tm(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(96)	87:13	—	—	192
$Ho(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(93)	83:17	—	—	192
$Eu(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(99)	73:17	—	—	192
$Sm(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(91)	70:30	—	—	192
$La(OTf)_3$ (10), 4 Å MS pwd.	CH_2Cl_2	rt	(87)	55:45	—	—	192
$Yb(OTf)_3$ (10), 4 Å MS pwd.	$CHCl_3$	rt	(79)	90:10	—	—	192
$Yb(OTf)_3$ (10), 4 Å MS pwd.	DCE	rt	(89)	90:10	—	—	192

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

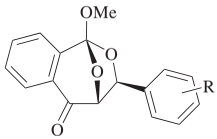
B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9  (*Continued*)		$Rh_2(OAc)_4$ (2 mol %), additive(s), 1 h	 **I** +  **II**	

Additive(s) (mol %)	Solvent	Temp	**I** + **II**	**I**/**II**	er **I**	er **II**	
$Yb(OTf)_3$ (10), 4 Å MS pwd.	C_6H_6	rt	(67)	79:21	—	—	192
$Yb(OTf)_3$ (10), 4 Å MS pwd.	THF	rt	(7)	60:40	—	—	192
$Yb(OTf)_3$ (10), 4 Å MS pwd.	Et_2O	rt	(89)	97:3	—	—	192
16a/$Sc(OTf)_3$ (10), 4 Å MS	CH_2Cl_2	−10°	(28)	60:40	57.0:43.0	51.5:48.5	100

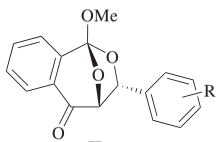


Catalyst, additive(s), solvent



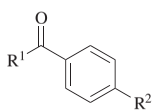
I

+

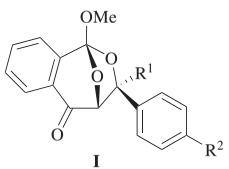


II

R	Catalyst (mol %)	Additive(s) (mol %)	Solvent	Temp	Time (h)	**I**	er **I**	**II**	er **II**	**I** + **II**	
H	$Cu(acac)_2$	—	C_6H_6	80°	~1	—	—	—	—	(82)	318
4-Cl	$Cu(acac)_2$	—	C_6H_6	80°	~1	(43)	—	(42)	—	—	318, 319
2,4-Cl_2	$Cu(acac)_2$	—	C_6H_6	80°	—	(12)	—	(75)	—	—	318, 319
2,6-Cl_2	$Cu(acac)_2$	—	C_6H_6	80°	—	(6)	—	(62)	—	—	318, 319
3-O_2N	$Cu(acac)_2$	—	C_6H_6	80°	—	(35)	—	(61)	—	—	318, 319
4-O_2N	$Cu(acac)_2$	—	C_6H_6	80°	—	(33)	—	(53)	—	—	318, 319
4-O_2N	$Rh_2(OAc)_4$ (2)	4 Å MS pwd.	CH_2Cl_2	rt	1	(23)	—	(70)	—	—	192
4-O_2N	$Rh_2(OAc)_4$ (2)	$Yb(OTf)_3$ (10), 4 Å MS pwd.	Et_2O	rt	1	(81)	—	(18)	—	—	192
4-O_2N	**9c**	—	$PhCF_3$	0	—	(24)	<50.5:49.5	(39)	53.0:47.0	—	99
4-MeO	$Cu(acac)_2$	—	C_6H_6	80°	~1	(43)	—	(33)	—	—	318, 319
4-MeO	$Rh_2(OAc)_4$ (2)	4 Å MS pwd.	CH_2Cl_2	rt	1	(31)	—	(37)	—	—	192
4-MeO	$Rh_2(OAc)_4$ (2)	$Yb(OTf)_3$ (10), 4 Å MS pwd.	Et_2O	rt	1	(67)	—	(10)	—	—	192



$Cu(acac)_2$, C_6H_6, 80°



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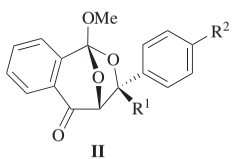


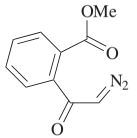
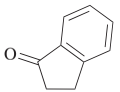
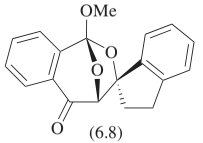
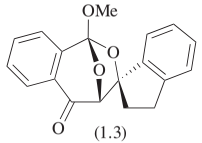
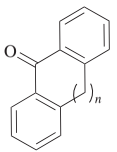
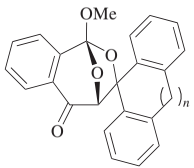
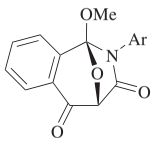
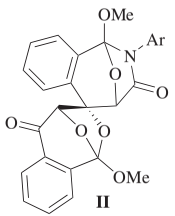
II

318

R^1	R^2	**I**	**II**
Me	H	(15)	(18)
Me	MeO	(7)	(6)
Me	O_2N	(29)	(46)
NC	O_2N	(86)	(7)
NC	MeO	(64)	(3)

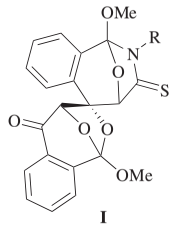
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Cu(acac)_2$, C_6H_6, 80°	 (6.8) +  (1.3)	318
		$Cu(acac)_2$, C_6H_6, 80°	 n: 0 (75); 1 (21)	318
		$Cu(acac)_2$, C_6H_6, 80°	 **I** +  **II**	198

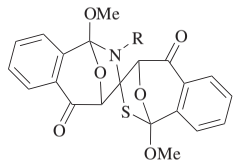
Ar	I	II
Ph	(0)	(32)
4-$O_2NC_6H_4$	(4)	(44)

$Cu(acac)_2$, C_6H_6, 80°



I

+



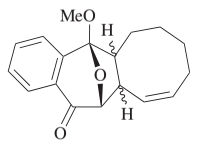
II

199

+ 3:1 adduct **III**
+ 4:1 adduct **IV**
+ 5:1 adduct **V**

R	I	II	III	IV	V
Me	(1.6)	(—)	(1.0)	(—)	(—)
Ph	(3.2)	(—)	(4.1)	(6.4)	(—)
4-ClC_6H_4	(11.2)	(—)	(—)	(13.7)	(9.4)
4-$O_2NC_6H_4$	(20.0)	(5.6)	(12.7)	(—)	(—)
4-$MeOC_6H_4$	(—)	(—)	(3.0)	(4.9)	(—)
4-MeC_6H_4	(3.7)	(—)	(3.5)	(5.3)	(1.8)

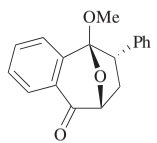
$Cu(acac)_2$, C_6H_6, 80°



(18)

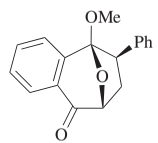
150, 317

$Rh_2(OAc)_4$ (2 mol %), ligand **16c**/$Eu(OTf)_3$ (10 mol %), 4 Å MS, MeOH (10 mol %), CH_2Cl_2, reflux



I

+



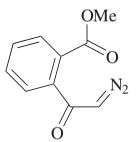
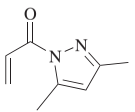
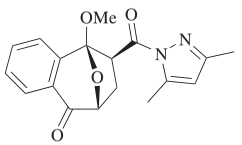
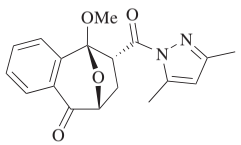
II

104

I + **II** (22) dr 69:31
er major 55.0:45.0
er minor 60.0:40.0

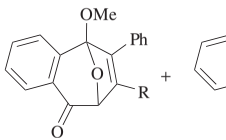
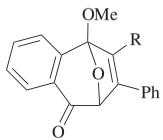
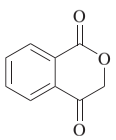
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

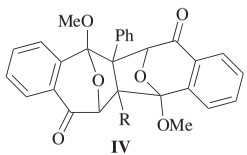
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Rh_2(OAc)_4$ (2 mol %), M(OTf)$_3$, 4 Å MS, CH_2Cl_2, rt	 **I** +  **II**	140

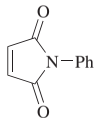
M (mol %)	I + II	I/II
—	(86)	23:77
Sc (10)	(67)	34:66
Lu (10)	(61)	56:44
Yb (10)	(79)	67:33
Yb (30)	(64)	80:20
Ho (10)	(92)	49:51
Eu (10)	(92)	34:66
Sm (10)	(97)	27:73
La (10)	(95)	28:72

Cu(acac)$_2$, 80°

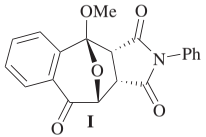
 **I** +  **II** +  **III** 185

R	Solvent	Time (h)	I	II	III	IV
H	C_6H_6	2	(9)	(0)	(20)	(—)
H	≡—Ph	—	(45)	(13)	(8)	(5)
MeO_2C	C_6H_6	2	(0)	(6)	(58)	(—)
MeO_2C	MeO_2C—≡—Ph	—	(9)	(39)	(7)	(—)

+  **IV**



Catalyst



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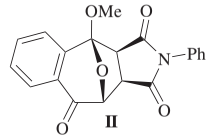
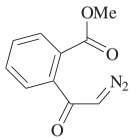
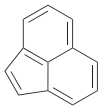
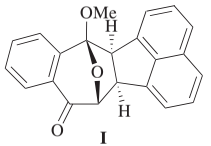
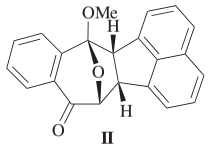
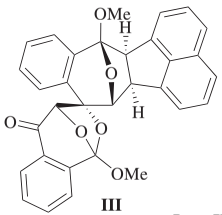
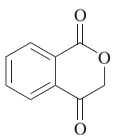


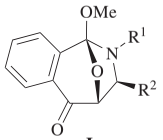
Catalyst (mol %)	Additive (mol %)	Solvent	Temp	**I** + **II**	**I**/**II**	er **I**	er **II**	
CuOTf (5)	—	C_6H_6	rt	(60)	63:37	—	—	56, 322
CuOTf (20)	—	C_6H_6	rt	(25)	75:25	—	—	56
$Cu(acac)_2$ (5)	—	C_6H_6	rt	(51)	21:79	—	—	56
$Cu(acac)_2$ (5)	—	C_6H_6	80°	(87)	33:67	—	—	321
CuI (20)	—	C_6H_6	rt	(31)	20:80	—	—	56
CuCl (5)	$Yb(OTf)_3$ (5)	C_6H_6	reflux	(43)	77:23	—	—	56, 322
CuCl (5)	$Yb(OTf)_3$ (5)	MeCN	reflux	(21)	90:10	—	—	56, 322
$Rh_2(OAc)_4$ (5)	—	C_6H_6	reflux	(88)	40:60	—	—	56
$Rh_2(OAc)_4$ (2)	$Yb(OTf)_3$ (10)	CH_2Cl_2	rt	(57)	54:46	—	—	56
$Rh_2(OAc)_4$ (2)	$Yb(OTf)_3$ (10)	Et_2O	rt	(10)	92:8	—	—	56
$Rh_2(OAc)_4$ (2)[i]	$Yb(OTf)_3$ (10)	Et_2O	rt	(89)	78:22	—	—	56
$Rh_2(OAc)_4$ (2)	$Sc(OTf)_3$ (10)	CH_2Cl_2	rt	(50)	84:16	—	—	56
$Rh_2(OAc)_4$ (2)[i]	$Sc(OTf)_3$ (10)	CH_2Cl_2	rt	(82)	49:51	—	—	56
15•CuOTf (5)	—	C_6H_6	rt	(83)	43:57	53.0:47.0	50.0:50.0	56, 322
15•CuOTf (10)	—	C_6H_6	rt	(61)	47:53	52.0:48.0	50.0:50.0	56
15•CuOTf (20)[s]	—	C_6H_6	rt	(43)	61:39	57.5:42.5	50.0:50.0	56
15•CuOTf (20)	—	C_6H_6	rt	(53)	37:63	57.5:42.5	50.0:50.0	56, 322
15•CuOTf (20)[t]	—	C_6H_6	rt	(53)	42:58	52.5:47.5	50.0:50.0	56
15•CuOTf (20)[u]	—	C_6H_6	rt	(72)	41:59	51.5:48.5	50.0:50.0	56
15•CuOTf (20)	—	C_6H_6/hexane 1:1	rt	(30)	45:55	59.0:41.0	50.0:50.0	56
15•CuOTf (100)	—	C_6H_6	rt	(37)	50:50	58.5:41.5	50.0:50.0	56
(*S*)-**6**	—	C_6H_6	rt	(45)	11:89	60.0:40.0	52.5:47.5	56, 322
$Rh_2(OAc)_4$ (2), **25** (10)	—	CH_2Cl_2	rt	(97)	44:56	51.0:49.0	50.5:49.5	56

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

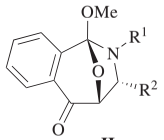
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Cu(acac)_2$, C_6H_6, 80°	 **I** +  **II** +  **III** +  **IV**	
			I **II** **III** **IV** (16) (25) (26) (—)	324
			(9) (13) (—) (14)	321

$Rh_2(OAc)_4$ (2 mol %),
L. A. (10 mol %),
4 Å MS, CH_2Cl_2, rt



I

+



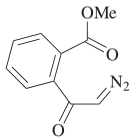
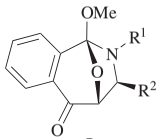
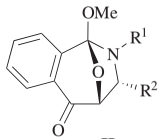
II

44

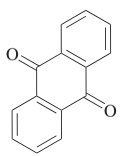
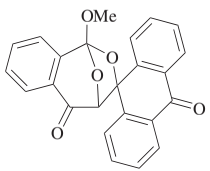
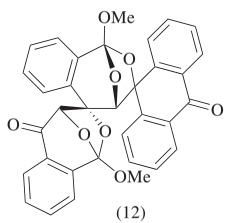
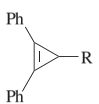
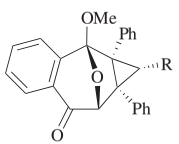
R^1	R^2	L. A.	Time (h)	**I** + **II**	**I/II**
Cy	Cy	$Yb(OTf)_3$	1 + 5[v]	(31)	12:88
Cy	Ph	$Yb(OTf)_3$	1	(21)	81:19
Ph	Cy	$Yb(OTf)_3$	11 + 13[v]	(47)	84:16
Ph	Ph	$Yb(OTf)_3$	1	(84)	62:38
Ph	4-ClC_6H_4	$Yb(OTf)_3$	1	(62)	73:27
Ph	2-$MeOC_6H_4$	$Yb(OTf)_3$	1	(94)	85:15
Ph	4-$MeOC_6H_4$	$Yb(OTf)_3$	1	(75)	77:23
Ph	2-$BnOC_6H_4$	Et_2AlCl	1	(4)	73:27
Ph	2-$BnOC_6H_4$	$SnCl_2$	1	(72)	88:12
Ph	2-$BnOC_6H_4$	$ZnCl_2$	1	(74)	94:6
Ph	2-$BnOC_6H_4$	$Mg(OTf)_2$	1	(36)	94:6
Ph	2-$BnOC_6H_4$	$Sc(OTf)_2$	1	(76)	90:10
Ph	2-$BnOC_6H_4$	$Yb(OTf)_3$	1	(92)	92:8
Ph	2-$BnOC_6H_4$	$La(OTf)_3$	1	(89)	94:6
4-ClC_6H_4	Ph	$Yb(OTf)_3$	1	(42)	76:24
2-$MeOC_6H_4$	Ph	$Yb(OTf)_3$	1	(72)	84:16
2-$MeOC_6H_4$	Ph	$Tm(OTf)_2$	1	(85)	88:12
2-$MeOC_6H_4$	Ph	$Ho(OTf)_3$	1	(72)	87:13
2-$MeOC_6H_4$	Ph	$Eu(OTf)_3$	1	(56)	88:12
2-$MeOC_6H_4$	Ph	$Sm(OTf)_3$	1	(44)	89:11

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

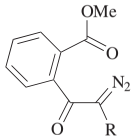
B. PYRYLIUMS (*Continued*)

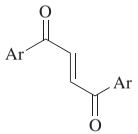
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
 (*Continued*)		$Rh_2(OAc)_4$ (2 mol %), L. A. (10 mol %), 4 Å MS, CH_2Cl_2, rt	 **I** +  **II**	44

R^1	R^2	L. A.	Time (h)	I + II	I/II
2-$MeOC_6H_4$	Ph	$La(OTf)_3$	1	(52)	89:11
2-$MeOC_6H_4$	Ph	$Sc(OTf)_3$	1	(42)	90:10
2-$MeOC_6H_4$	Ph	$Yb(OTf)_3$	1	(76)	88:12
Ph_2CH	EtO_2C	$Yb(OTf)_3$	1	(45)	58:42

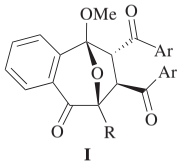
		$Cu(acac)_2$, C_6H_6, 80°	 (17) +  (12)	318, 320
		$Rh_2(OAc)_4$, CH_2Cl_2, rt		148

R	
H	(92)
Me	(76)
MeO_2C	(5)
CH_2=CH	(70)
Ph	(67)

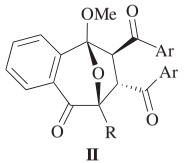




$Cu(acac)_2$, C_6H_6, 80°

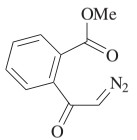


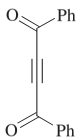
+



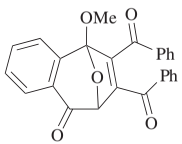
I **II**

R	Ar	I	II	
H	Ph	(83)	(6)	321
H	4-MeC_6H_4	(75)	(—)	150
D	Ph	(70)	(—)	321

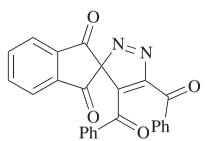




$Cu(acac)_2$, C_6H_6, 80°

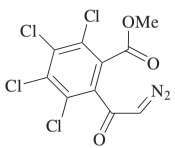


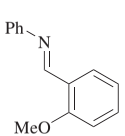
+



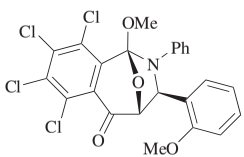
185

(66) (10)

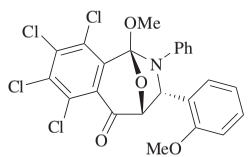




$Rh_2(OAc)_4$ (2 mol %),
4 Å MS, L. A.,
CH_2Cl_2, rt, 1 h



+



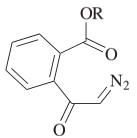
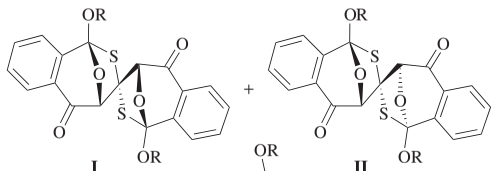
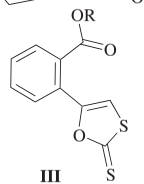
44

I **II**

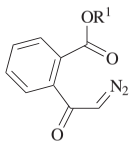
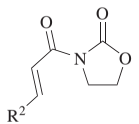
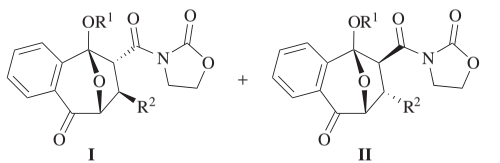
L. A.	I + II	I/II
—[w]	(40)[x]	85:15
$Yb(OTf)_3$ (10 mol %)	(83)	87:13

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

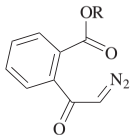
B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	CS_2	$Rh_2(OAc)_4$, C_6H_6, 46–80°	 **I** + **II**  **III**	201

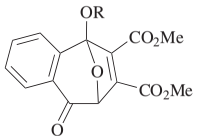
R	I	II	III
Me	(64.5)	(10.8)	(6.3)
i-Pr	(65.7)	(8.8)	(8.8)

		$Rh_2(OAc)_4$ (2 mol %), ligand/$M(OTf)_3$ (*x* mol %), 4 Å MS, CH_2Cl_2, rt	 **I** + **II**	102

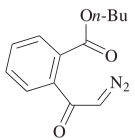
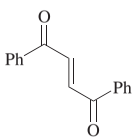
R^1	R^2	Ligand	M	*x*	Temp	I + II	I/II	er I
i-Pr	Me	**16c**	Yb	10	rt	(39)	88:12	54.0:46.0
4-$BrC_6H_4CH_2$	Me	**16b**	Yb	10	rt	(40)	>99:1	92.0:8.0
4-$BrC_6H_4CH_2$	Me	**16b**	Tm	10	rt	(51)	>99:1	86.0:14.0
4-$BrC_6H_4CH_2$	Me	**16c**	Yb	10	rt	(57)	>99:1	90.5:9.5
4-$BrC_6H_4CH_2$	Me	**16c**	Yb	20	rt	(60)	>99:1	98.0:2.0
4-$BrC_6H_4CH_2$	Me	**16c**	Yb	30	rt	(25)	>99:1	96.0:4.0
4-$BrC_6H_4CH_2$	EtO_2C	**16c**	Yb	10	rt	(15)	<1:99	78.0:22.0
4-$BrC_6H_4CH_2$	EtO_2C	**16c**	Yb	20	reflux	(15)	<1:99	83.0:17.0



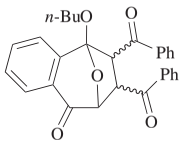

Catalyst, C_6H_6



R	Catalyst	Temp		
CH_2=$CHCH_2$	$Rh_2(OAc)_4$	rt	(84)	209
n-Bu	$Cu(acac)_2$	80°	(80)	150
CH_2=$CHCH_2CH_2$	$Rh_2(OAc)_4$	rt	(70)	208, 209
CH_2=$C(Me)CH_2CH_2$	$Rh_2(OAc)_4$	rt	(65)	208, 209
Bn	$Rh_2(OAc)_4$	rt	(74)	209

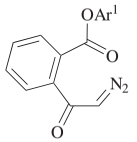
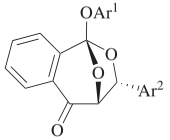
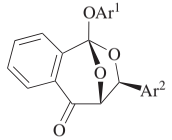
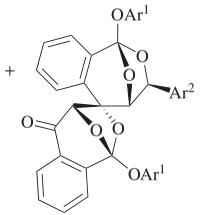
$Cu(acac)_2$, C_6H_6, 80°



(92) 150

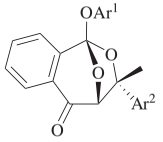
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9  $Ar^1 = 4\text{-}MeOC_6H_4$		$Cu(acac)_2$, C_6H_6, 80°	 **I** +  **II** +  **III**	

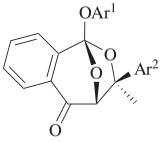
Ar^2	**I**	**II**	**III**	Refs.
Ph	(43)	(38)	(11)	320
Ph	(52)	(43)	(—)	318
$4\text{-}O_2NC_6H_4$	(60)	(36)	(0.6)	320
$4\text{-}O_2NC_6H_4$	(47)	(45)	(—)	318
$4\text{-}MeOC_6H_4$	(35)	(21)	(25)	318, 320

$Cu(acac)_2$, C_6H_6, 80°



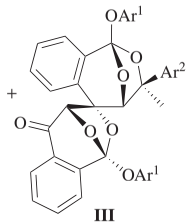
I

+



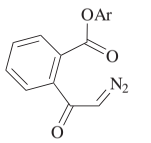
II

318, 320

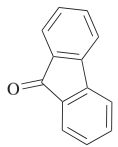


III

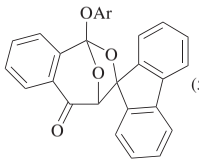
Ar^2	I	II	III
Ph	(13)	(8)	(5)
$4\text{-}O_2NC_6H_4$	(29)	(54)	(11)
$4\text{-}MeOC_6H_4$	(4)	(0)	(1)



$Ar = 4\text{-}MeOC_6H_4$



$Cu(acac)_2$, C_6H_6, 80°



(53)

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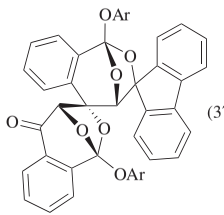
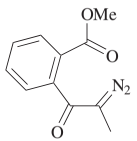
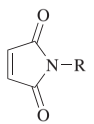


(37)

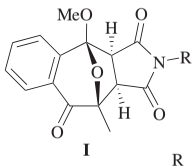
318, 320

C_{10}



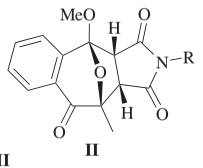


$Cu(acac)_2$, C_6H_6, 80°



I

+

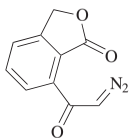
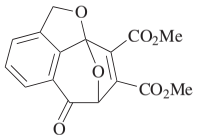
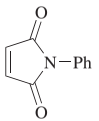
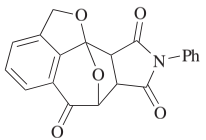
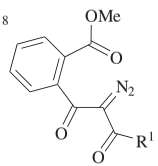
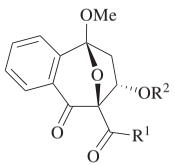


II

R	I	II	
Me	(54)	(41)	321, 323
Et	(66)	(28)	321
Ph	(57)	(39)	321

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

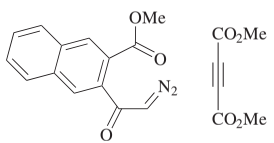
B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (85)	209, 325
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (79)	209, 325
C_{12-18} 		$Rh_2(OAc)_4$ (2 mol %), co-catalyst (10 mol %), 4 Å MS		

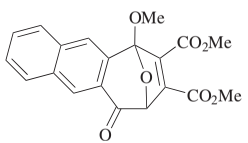
R^1	R^2	Co-catalyst	Solvent	Temp		er	
Et	Cy	**24b**/$Ni(ClO_4)_2$•$6H_2O$	CH_2Cl_2	reflux	(77)	86.5:13.5	104
n-Pr	TBS	**24b**/$Ni(ClO_4)_2$•$6H_2O$	CH_2Cl_2	reflux	(44)	53.0:47.0	104
n-Pr	TBS	**16c**/$EuOTf)_3$	CH_2Cl_2	reflux	(68)	59.5:40.5	104
n-Pr	*n*-Bu	**24a**/$Ni(ClO_4)_2$•$6H_2O$	CH_2Cl_2	rt	(78)	79.5:20.5	103, 104
n-Pr	*n*-Bu	**24b**/$Ni(ClO_4)_2$•$6H_2O$	CH_2Cl_2	rt	(86)	86.5:13.5	103, 104
n-Pr	*n*-Bu	**24b**/$Ni(ClO_4)_2$•$6H_2O$	CH_2Cl_2	reflux	(99)	96.0:4.0	103, 104
n-Pr	*n*-Bu	**24c**/$Ni(ClO_4)_2$•$6H_2O$	CH_2Cl_2	rt	(86)	71.0:29.0	103, 104
n-Pr	*n*-Bu	**16c**/$EuOTf)_3$	CH_2Cl_2	reflux	(89)	72.0:28.0	103

n-Pr	*n*-Bu	**16c**/Yb(OTf)$_3$	$CHCl_3$	reflux	(71)	72.5:27.5	103
n-Pr	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(96)	96.5:3.5	103, 104
n-Pr	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux[a]	(85)	95.0:5.0	104
n-Pr	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux[a,b]	(80)	97.0:3.0	104
n-Pr	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux[a,b,c]	(86)	96.5:3.5	104
n-Pr	Bn	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(76)	89.5:10.5	104
i-Pr	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(96)	98.5:1.5	103, 104
i-Pr	Bn	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(85)	95.0:5.0	104
n-Bu	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(87)	96.5:3.5	103, 104
i-Bu	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(82)	94.0:6.0	103, 104
n-C_5H_{11}	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(66)	92.0:8.0	103, 104
Cy	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(78)	98.0:2.0	103, 104
Bn	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(85)	96.0:4.0	103, 104
$PhCH_2CH_2$	Cy	**24b**/Ni(ClO$_4$)$_2$•6H$_2$O	CH_2Cl_2	reflux	(87)	88.5:11.5	103, 104

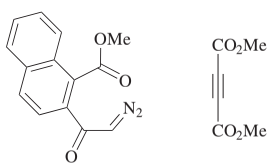
C_{13}



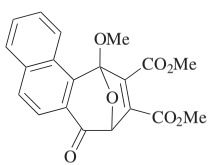
Catalyst **8d**, $PhCF_3$, rt



(71) er 96.5:3.5 98



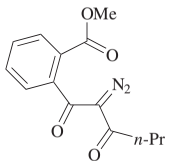
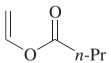
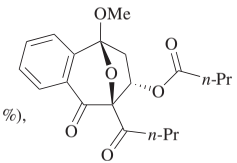
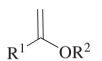
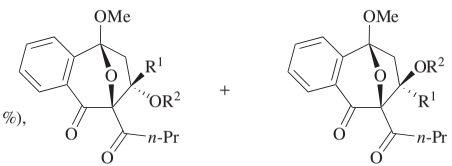
Catalyst **8d**, $PhCF_3$, rt



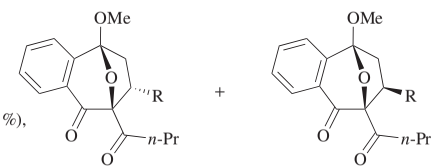
(27) er 78.5:21.5 98

TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

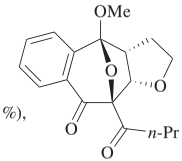
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 		$Rh_2(OAc)_4$ (2 mol %), ligand **24b/** $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), 4 Å MS, CH_2Cl_2, reflux	 (2) er 50.5:49.5	104
		$Rh_2(OAc)_4$ (2 mol %), ligand **24b/** $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), 4 Å MS, CH_2Cl_2, reflux	 **I** + **II**	104

R^1	R^2	I + II	I/II	er I	er II
Me	Me	(85)	61:39	65.0:35.0	58.5:41.5
Ph	*n*-Bu	(68)	74:26	72.0:28.0	72.0:28.0
TBSO	*n*-Bu	(12)	74:26	51.0:49.0	—

			$Rh_2(OAc)_4$ (2 mol %), ligand **24b/** $Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %), 4 Å MS, reflux	 **I** + **II**	104

R	Solvent	I	er I	II
$BuOCH_2$	CH_2Cl_2	(1)	—	(—)
n-Bu	CH_2Cl_2	(9)	52.0:48.0	(—)
Ph	CH_2Cl_2	(34)[y]	53.5:46.5	(4)
Ph	$CHCl_3$	(8)	55.0:45.0	(1)

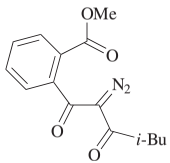
$Rh_2(OAc)_4$ (2 mol %),
ligand **24b/**
$Ni(ClO_4)_2 \cdot 6H_2O$ (10 mol %),
4 Å MS, $CHCl_3$



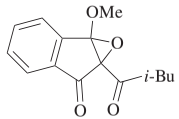
Temp (°)		er
40	(95)	85.0:15.0
45	(98)	85.0:15.0

104

C_{14}



$Rh_2(OAc)_4$ (2 mol %), rt



(92)

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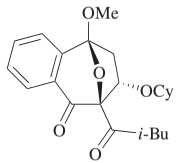
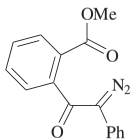
Ligand **24b/**
$Ni(ClO_4)_2 \cdot 6H_2O$
(10 mol %), 4 Å MS,
CH_2Cl_2, reflux

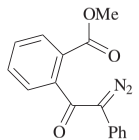


	er
(61)[z]	54.5:45.5
(40)[aa]	82.5:17.5
(60)[bb]	93.0:7.0

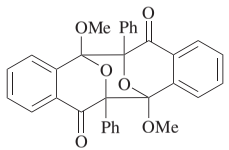
104

C_{15}





$Rh_2(OAc)_4$, toluene, 80°



(87)

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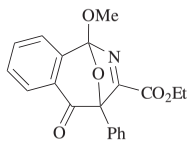
$Rh_2(OAc)_4$, toluene, 110°



(97)

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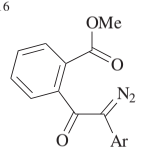
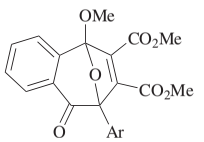
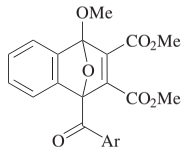
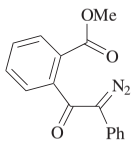
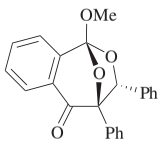
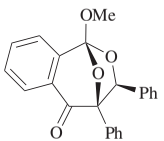
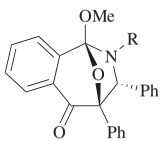
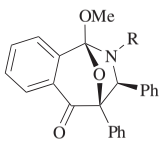
TABLE 13. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM ESTERS (*Continued*)

B. PYRYLIUMS (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15-16} 		Catalyst	 **I** +  **II**	119
C_{15} 		$Rh_2(OAc)_4$, toluene, 110°	 **I** +  **II**	119
		$Rh_2(OAc)_4$, toluene, 110°	 **I** +  **II**	119

Ar	Catalyst	Solvent	Temp (°)	I	II	I/II
Ph	$Rh_2(OAc)_4$	toluene	80	(91)	(—)	—
2-$MeO_2CC_6H_4$	$Rh_2(OAc)_4$	toluene	110	(17)	(68)	—
2-$MeO_2CC_6H_4$	$Rh_2(tfa)_4$	—	—	(—)	(—)	1:2
2-$MeO_2CC_6H_4$	$Rh_2(cap)_4$	—	—	(5)	(78)	—

I + **II** (90), **I/II** = 2:1

R	I + II	I/II
Me	(90)	2:1
PhO_2S	(90)	8:1

[a] Dried and purified CH_2Cl_2 (via distillation with $CaCl_2$ then CaH_2) was used.

[b] MeOH (10 mol %) was used as an additive.

[c] A mixture of diazo compound and dipolarophile in CH_2Cl_2 was added over a period of 1 hour.

[d] The second step of the reaction was carried out at −25°.

[e] The concentration of catalyst **16a**/$Lu(OTf)_3$ was 2.5×10^{-3} M.

[f] The concentration of catalyst **16a**/$Lu(OTf)_3$ was 10.0×10^{-3} M.

[g] Catalyst **16a**/$Sc(OTf)_3$ was prepared in the presence of CF_3CO_2H.

[h] CF_3CO_2H was added before the addition of $Rh_2(OAc)_4$ and the carbonyl compound.

[i] The reaction was carried out in the presence of 4 Å MS.

[j] The reaction time was 5 hours.

[k] The reaction time was 3 hours.

[l] The addition time of the diazo compound was 1 hour.

[m] The catalyst complex was prepared in CH_2Cl_2 in the presence of 4 Å MS for 2 hours.

[n] The catalyst complex was prepared in CH_2Cl_2 in the absence of 4 Å MS for 2 hours and the mixture was then stirred with 4 Å MS for 2 hours.

[o] The catalyst complex was prepared in CH_2Cl_2 in the absence of 4 Å MS for 2 hours.

[p] The catalyst complex was prepared in CH_2Cl_2 in the absence of 4 Å MS for 1 hour and the mixture was then stirred with 4 Å MS for 2 hours.

[q] The catalyst complex was prepared in CH_2Cl_2 in the absence of 4 Å MS for 1 hour and then aged with 4 Å MS and the carbonyl compound for 2 hours.

[r] The yields are based on several runs.

[s] One equivalent of *N*-phenylmaleimide was used.

[t] Three equivalents of *N*-phenylmaleimide were used.

[u] Five equivalents of *N*-phenylmaleimide were used.

[v] After adding the diazo compound, the mixture was stirred for an additional 13 or 5 hours at room temperature.

[w] After adding the diazo compound, the mixture was stirred for an additional 95 hours at room temperature.

[x] Twenty-six percent of the diazo substrate was recovered.

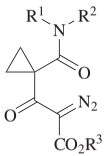
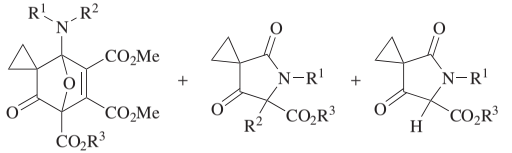
[y] $Ni(BF_4)_2 \bullet 6H_2O$ was used for the preparation of the catalyst **24b** complex.

[z] The reaction was carried out by slow addition of the substrates.

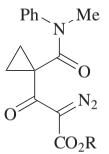
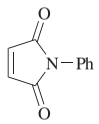
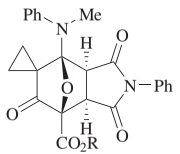
[aa] The reaction was carried out by slow addition of the intermediate epoxyindanone over 1 hour into a solution of the dipolarophile and Ni catalyst in commercial-grade CH_2Cl_2.

[bb] The reaction was carried out by slow addition of the intermediate epoxyindanone over 1 hour into a solution of the dipolarophile and Ni catalyst in dry CH_2Cl_2.

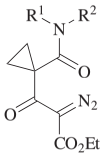
TABLE 14. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM AMIDES

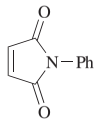
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		Catalyst		

I **II** **III**

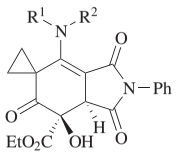
R^1	R^2	R^3	Catalyst	Solvent	Temp (°)	I	II	III	Refs.
Me	Bn	Et	$Rh_2(pfb)_4$	—	—	(57)	(23)	(—)	155
Me	Bn	Et	$Rh_2(OAc)_4$	C_6H_6	80	(57)	(23)	(—)	111
Me	Bn	Et	$Rh_2(OAc)_4$	C_6H_6	80	(57)	(42)	(—)	37
Et	Et	Et	$Rh_2(pfb)_4$	—	—	(40)	(—)	(27)	155
Et	Et	Et	$Rh_2(OAc)_4$	C_6H_6	80	(92)	(—)	(8)	37
t-Bu	Bn	Et	$Rh_2(OAc)_4$	C_6H_6	80	(69)	(—)	(—)	111
Ph	Me	Me	$Rh_2(OAc)_4$	C_6H_6	80	(87)	(—)	(—)	37
Ph	Me	Et	$Rh_2(OAc)_4$	C_6H_6	80	(87)	(—)	(—)	37
		$Rh_2(OAc)_4$, C_6H_6, 80°		37

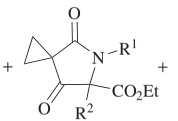
R	
Me	(80)
Et	(42)

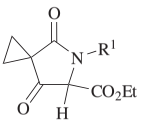




$Rh_2(OAc)_4$, C_6H_6, 80°





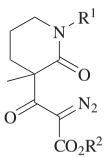


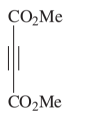
37

I **II** **III**

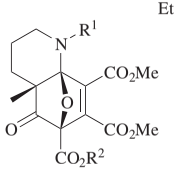
R^1	R^2	**I**	**II**	**III**
Me	Bn	(60)	(40)	(—)
Et	Et	(66)	(—)	(34)

C_9

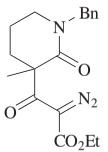


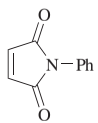


$Rh_2(OAc)_4$, C_6H_6, 80°

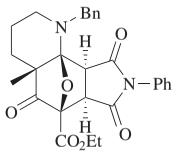


R^1	R^2		
CH_2=$CH(CH_2)_3$	Me	(78)	214
Bn	Et	(80)	



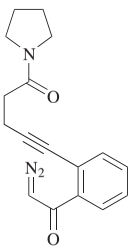


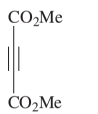
$Rh_2(OAc)_4$, C_6H_6, 80°



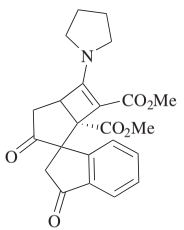
(83) 214

C_{13}





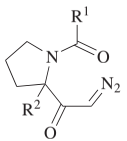
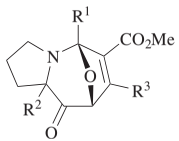
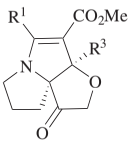
$Rh_2(oct)_4$, CH_2Cl_2, rt



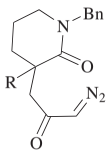
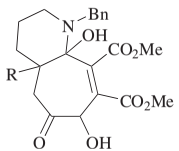
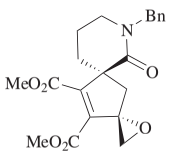
(70) dr 1:1 108, 107

TABLE 15. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM AMIDES

A. NON-AROMATIC YLIDES

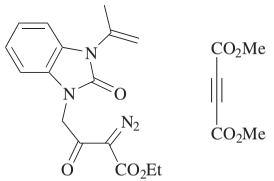
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-20} 		$Rh_2(OAc)_4$, C_6H_6	 **I** +  **II**	

R^1	R^2	R^3	Temp	**I**	**II**	Refs.
Me	H	H	50°	(5)	(90)	223
Ph	Bn	H	rt	(80)	(—)	223
MeO	H	MeO_2C	60°	(43)	(43)	223
Me	H	MeO_2C	rt	(10)	(87)	223, 224
Me	D	MeO_2C	rt	(45)	(—)	223
Ph	Me	MeO_2C	rt	(70)	(—)	223
Ph	Bn	MeO_2C	rt	(95)	(—)	223, 224

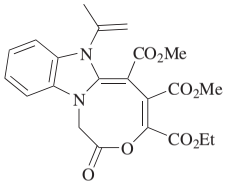
C_{8-9}   $Rh_2(OAc)_4$, CH_2Cl_2, rt  **I** +  **II**

R	**I**	**II**	Refs.
H	(53)	(25)	225
Me	(41)	(—)	

C_{11}



$Rh_2(OAc)_4$, C_6H_6, 80°



(33)

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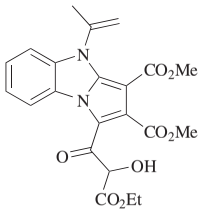
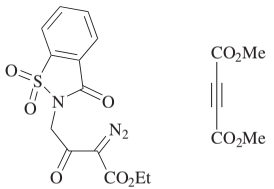
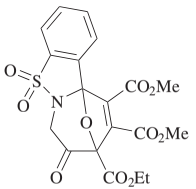


(24)

229



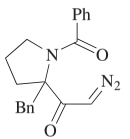
$Rh_2(OAc)_4$, CH_2Cl_2, rt

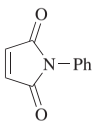


(61)

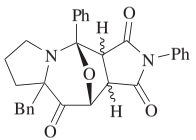
226, 228

C_{20}





$Rh_2(OAc)_4$, C_6H_6, rt

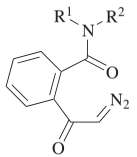
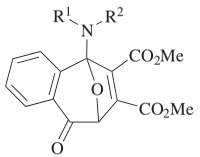


(70)

223

TABLE 15. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM AMIDES (*Continued*)

B. PYRYLIUMS

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		$Rh_2(OAc)_4$, C_6H_6, rt		225, 227 208, 209

R^1	R^2	
Me	EtO_2CCH_2	(90)
Bn	CH_2=$CHCH_2CH_2$	(65)

TABLE 16. INTERMOLECULAR CYCLOADDITIONS OF 7-MEMBERED-RING CARBONYL YLIDES FROM AMIDES

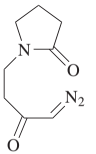
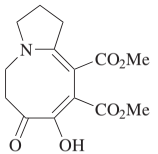
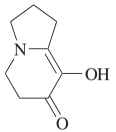
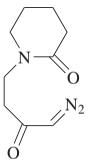
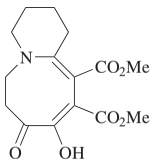
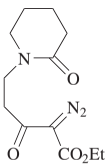
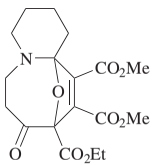
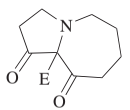
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		$Rh_2(OAc)_4$, $CHCl_3$, rt	 (40) +  (32)	111
C_9				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (67)	111
C_{10}				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (38) +  (22) E = EtO_2C	111

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES

A. NON-AROMATIC YLIDES

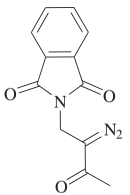
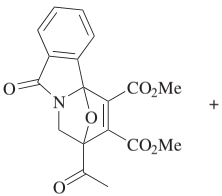
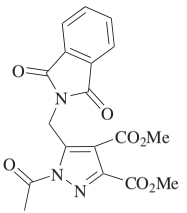
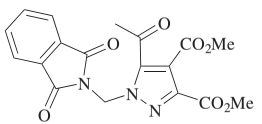
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		$Rh_2(OAc)_4$, CH_2Cl_2, pentane, rt	 (68) +  (21) +  (7)	120

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES

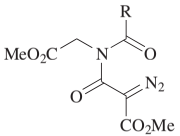
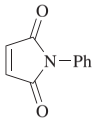
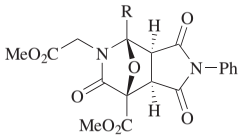
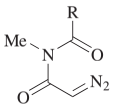
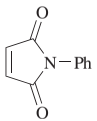
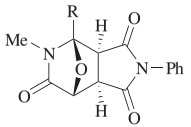
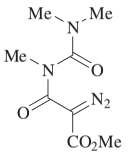
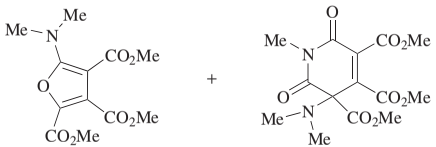
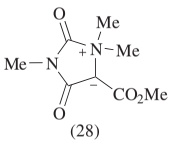
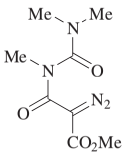
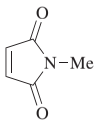
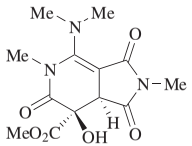
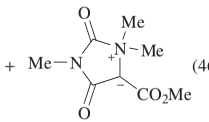
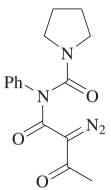
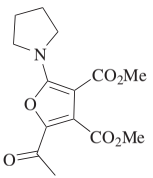
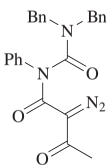
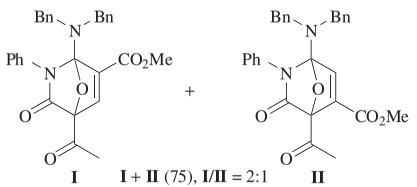
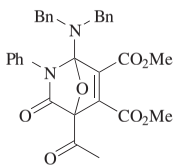
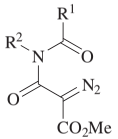
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-10} 		$Rh_2(pfbm)_4$, C_6H_6, 80°	 R: MeO (73); Ph (70); 4-$MeOC_6H_4$ (68); 4-$O_2NC_6H_4$ (67)	326
C_{4-5} 		$Rh_2(OAc)_4$, C_6H_6, 80°	 R: Me (—); Et (—)	184
C_4 		$Rh_2(OAc)_4$, toluene, 110°	 (25) + (18) +  (28)	37, 327

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

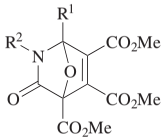
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$Rh_2(OAc)_4$, toluene, 110°	 (24) +  (46)	37
C_5 		$Rh_2(oct)_4$, C_6H_6, rt	 (100)	184
		$Rh_2(oct)_4$, C_6H_6, rt	 **I** **I** + **II** (75), **I**/**II** = 2:1 **II**	184
		$Rh_2(oct)_4$, C_6H_6, rt	 (47)	184

C_{5-7}

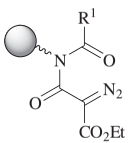


Catalyst

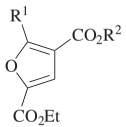


R^1	R^2	Catalyst	Solvent	Temp		
Me	CH_2=$CHCH_2$	$Rh_2(tfa)_4$	—	—	(—)	234
Me	CH_2=$CHCH_2$	$Rh_2(pfbm)_4$	—	—	(—)	234
Me	*i*-Bu	$Rh_2(pfbm)_4$	—	rt	(—)	234
Me	*i*-Bu	$Rh_2(OAc)_4$	—	—	(—)	234
Me	*i*-Bu	$Rh_2(tfa)_4$	—	—	(—)	234
Me	*i*-Bu	$Rh_2(pfbm)_4$	C_6H_6	rt	(81)	234
i-Pr	Me	$Rh_2(OAc)_4$	—	—	(—)	234
i-Pr	Me	$Rh_2(tfa)_4$	—	—	(—)	234
i-Pr	Me	$Rh_2(pfbm)_4$	—	—	(—)	234

C_{5-12}



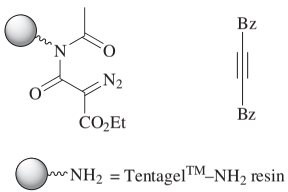
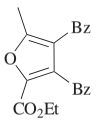
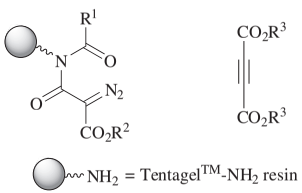
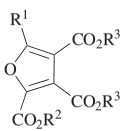
$Rh_2(OAc)_4$, C_6H_6, 80°



R^1	R^2		
Me	Me	(56)	232
$Ph(CH_2)_2$	Et	(51)	

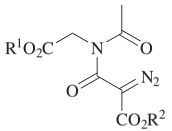
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

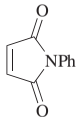
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		$Rh_2(OAc)_4$, C_6H_6, 80°	 (50)	232
C_{5-13} 		$Rh_2(OAc)_4$, C_6H_6, 80°		232

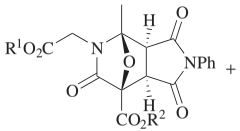
R^1	R^2	R^3	
Me	Me	Me or Et	(—)
Me	Et	Me	(70)
Me	Et	Et	(—)
$^{13}CH_3$	Et	Me	(67)
i-Pr	Me or Et	Me or Et	(—)
$Ph(CH_2)_2$	Me	Me or Et	(—)
$Ph(CH_2)_2$	Et	Me	(58)
$Ph(CH_2)_2$	Et	Et	(62)
$Cy(CH_2)_3$	Me or Et	Me or Et	(—)
n-C_9H_{19}	Me or Et	Me or Et	(—)

C_5

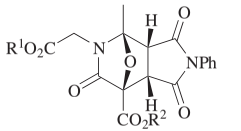




Catalyst



I



II

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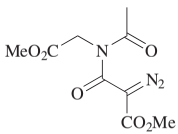
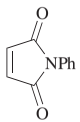
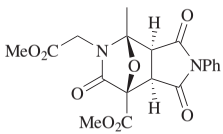
R^1	R^2	Catalyst	Solvent	Temp (°)	I	II
Me	Me	$Rh_2(OAc)_4$	MeCN	—	(50)	(—)
Me	Me	$Rh_2(OAc)_4$	$MeNO_2$	—	(90)	(—)
Me	Me	$Rh_2(pfbm)_4$	C_6H_6	80	(95)	(<3)
Me	*t*-Bu	$Rh_2(pfbm)_4$	C_6H_6	80	(85)	(—)
t-Bu	Me	$Rh_2(pfbm)_4$	C_6H_6	80	(66)	(—)

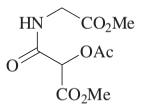




$Rh_2(pfbm)_4$, $Sc(OTf)_3$, C_6H_6, 80°



(38) +

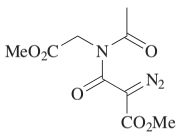
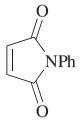
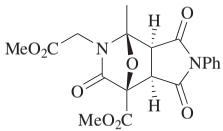
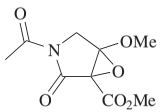


(26)

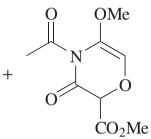
326, 328

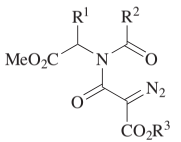
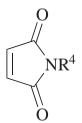
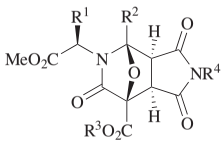
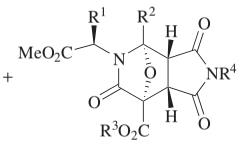
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		Catalyst	 +  **I** **II**	328

Catalyst	Solvent	Temp (°)	I	II	III
$Rh_2(pfbm)_4$	C_6H_6	80	(95)	(—)	(—)
$Rh_2(pfbm)_4$	CH_2Cl_2	rt	(95)	(—)	(—)
$Rh_2(pfb)_4$	C_6H_6	80	(95)	(—)	(—)
$Rh_2(tfa)_4$	C_6H_6	80	(95)	(—)	(—)
$Rh_2(OAc)_4$	C_6H_6	80	(3)	(90)	(3)
$Rh_2(cap)_4$	C_6H_6	80	(50)	(40)	(—)

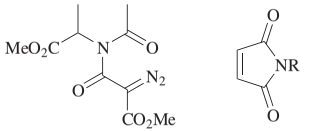
+  **III**

C_{5-10}   $Rh_2(pfbm)_4$, C_6H_6, 80°  +  90

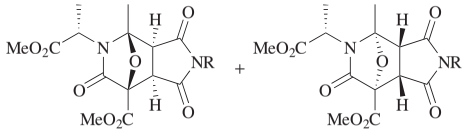
I **II**

R^1	R^2	R^3	R^4	I + II	I/II
Me	*i*-Pr	Me	Ph	(94)	80:20
Me	Ph	Me	Me	(84)	80:20
Me	Ph	Me	Ph	(80)	82:18
i-Bu	Me	Me	Ph	(90)	82:18
Bn	Me	Me	Ph	(89)	95:5
Bn	Me	Et	Me	(84)	95:5
Bn	Me	Et	Ph	(88)	95:5

C_5

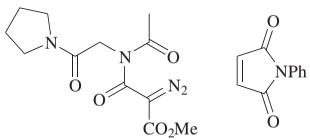


$Rh_2(pfbm)_4$, C_6H_6, 80°

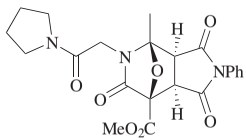


R	I + II	I/II
Me	(89)	17:83
Ph	(89)	12:88

90



$Rh_2(pfbm)_4$, C_6H_6, 80°



(89)

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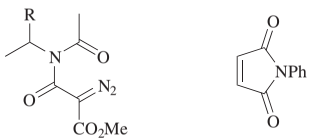
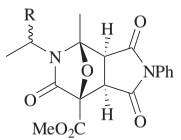
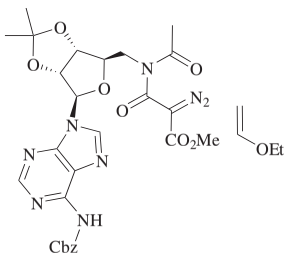


$Rh_2(pfbm)_4$, C_6H_6, 80°

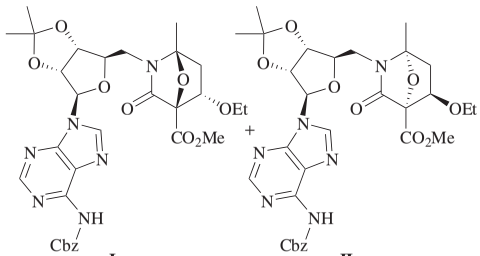


R		dr
Ph	(92)	55:45
1-naphthyl	(95)	60:40

90



$Rh_2(pfbm)_4$, toluene, 60°, 4 Å MS



I + **II** (70), **I**/**II** = 1:1

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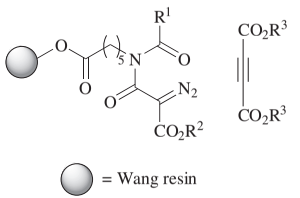
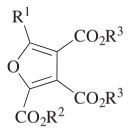
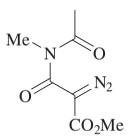
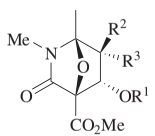
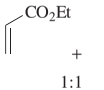
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

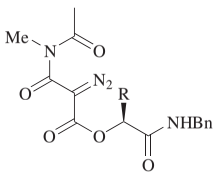
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-10} 		1. $Rh_2(pfbm)_4$, rt 2. C_6H_6, 79°		233, 234
C_5 		$Rh_2(pfbm)_4$		94

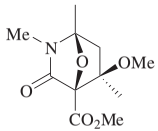
R^1	R^2	R^3				
Me	Me	Me	(70)			
Me	Et	Me or Et	(—)			
Me	*t*-Bu	Me or Et	(—)			
i-Pr	Me	Me or Et	(—)			
i-Pr	Et	Me or Et	(—)			
i-Pr	*t*-Bu	Me or Et	(—)			
Ph	Me	Me or Et	(—)			
Ph	Et	Me or Et	(—)			
Ph	*t*-Bu	Me or Et	(—)			

R^1	R^2	R^3	(*E*)/(*Z*)	Solvent	Temp (°)	
TMS	H	H	—	C_6H_6	80	(>98)
Me	*n*-C_6H_{13}	H	1:9	C_6H_6	100	(95)
Me	*n*-C_6H_{13}	H	3:2	C_6H_6	100	(97)
Et	H	H	—	C_6H_6	80	(>98)
t-Bu	H	H	—	C_6H_6	80	(>98)
i-C_5H_{11}	Me	Me	—	C_6H_5Cl	130	(82)
Cy	H	H	—	C_6H_6	80	(>98)
Ph	H	H	—	C_6H_6	80	(>98)
Bn	H	H	—	C_6H_6	80	(>98)



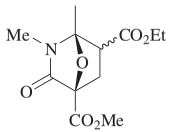


Rh$_2$(pfbm)$_4$, C$_6$H$_5$Cl, 130°



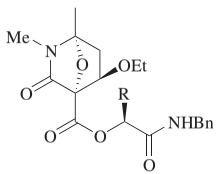
(16) + (48) 94

Rh$_2$(pfbm)$_4$, C$_6$H$_6$, 60°



(76) + (19) 94

Rh$_2$(pfbm)$_4$, CH$_2$Cl$_2$, rt, 4 Å MS



R		% de
Me	(90)	18
i-Pr	(96)	82
i-Bu	(94)	74
t-Bu	(95)	82
Bn	(96)	76

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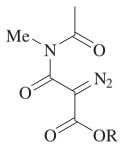
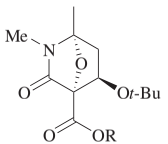
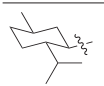
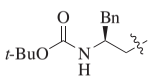
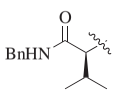
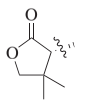
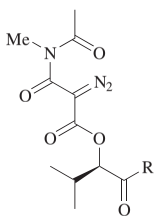
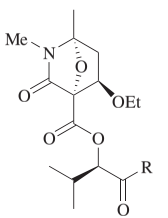
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

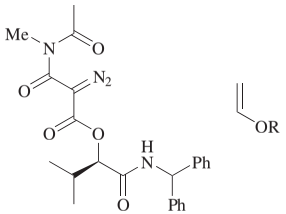
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		$Rh_2(pfbm)_4$, CH_2Cl_2, rt, 4 Å MS		91

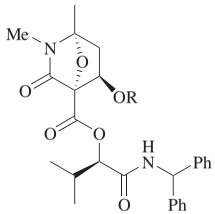
R		% de	R		% de
	(96)	32		(88)	0
	(93)	14		(96)	84
	(95)	12			

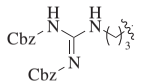
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Rh_2(pfbm)_4$, CH_2Cl_2, rt, 4 Å MS		91

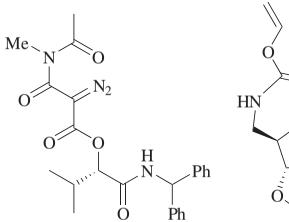
R		% de
BnO	(85)	12
Bn_2N	(89)	18
CyHN	(88)	78
(*S*)-Ph(Me)C(H)HN	(93)	90
(*R*)-Ph(Me)C(H)HN	(93)	92
$Ph(Me)_2CHN$	(91)	94
$Ph_2C(H)HN$	(92)	>95

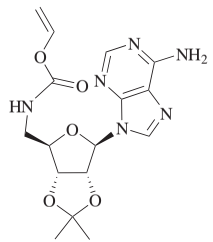


$Rh_2(pfbm)_4$, CH_2Cl_2, rt, 4 Å MS

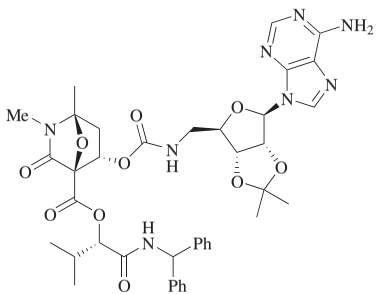


R		% de	
t-Bu	(95)	>95	
Cy	(92)	>95	
Bn	(88)	>95	91
	(86)	>95	





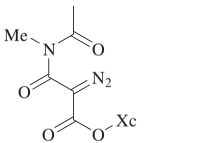
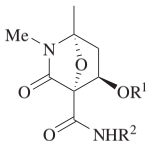
$Rh_2(pfbm)_4$, toluene, 80°, 4 Å MS

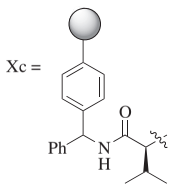


(69) 152

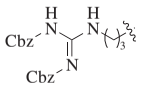
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

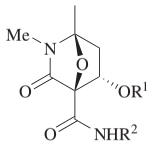
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5  		1. $Rh_2(pfbm)_4$, CH_2Cl_2, rt, 4 Å MS 2. R^2NH_2, solvent		329

Xc = 

= BHA resin

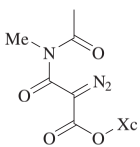
R^1	R^2	Solvent		er
Et	H	EtOH	(62)	—
Et	Me	THF	(64)	>97.5:2.5
Et	CH_2=$CHCH_2$	THF	(64)	—
Et	*i*-Pr	THF	(65)	—
Et	$CyCH_2$	THF	(60)	—
Et	(−)-myrtanyl	THF	(61)	—
Cy	Me	THF	(63)	96.5:3.5
	Me	THF	(49)	96.5:3.5
(−)-menthyl	Me	THF	(61)	>97.5:2.5 (dr)

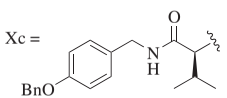
1. $Rh_2(pfbm)_4$, CH_2Cl_2, rt, 4 Å MS
2. R^2NH_2, THF



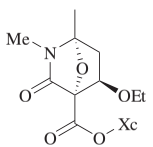
329

R^1	R^2		er
Et	HO[a]	(58)	—
Et	Me	(60)	97.0:3.0
Et	$HO(CH_2)_3$	(64)	—
Et	Bn	(61)	—
Et	3-indolylCH_2CH_2	(58)	—
Et	(−)-myrtenyl	(59)	—
t-Bu	Me	(65)	97.0:3.0
Bn	Me	(61)	97.0:3.0
(−)-menthyl	Me	(57)	>95.5:4.5 (dr)





$Rh_2(pfbm)_4$, CH_2Cl_2, rt, 4 Å MS



(83) dr 91:9

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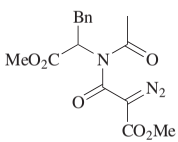
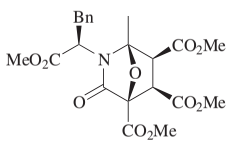


$Rh_2(pfbm)_4$, C_6H_6, 80°

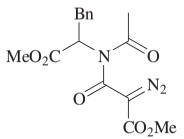
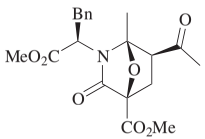
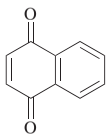
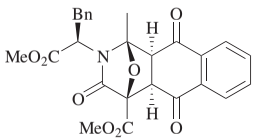
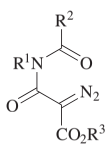
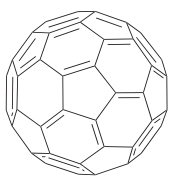
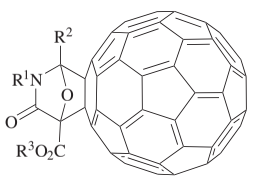


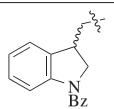
(79) dr 95:5

90

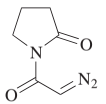
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

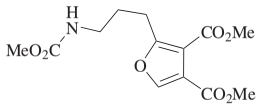
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		$Rh_2(pfbm)_4$, C_6H_6, 80°	 (90) dr 95:5	90
		$Rh_2(pfbm)_4$, C_6H_6, 80°	 (88) dr 95:5	90
C_{5-17} 		$Rh_2(pfb)_4$, 1,2-$Cl_2C_6H_4$, 90°		144

R^1	R^2	R^3	dr
Me		Me (48)	2.1:1
$PhCH_2CH_2$	Me	*t*-Bu (24)	—

C_6



1. $Rh_2(OAc)_4$, C_6H_6, 80°
2. MeOH, reflux



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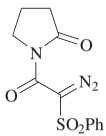
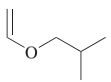
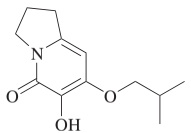




$Rh_2(OAc)_4$, C_6H_6, reflux



(64)

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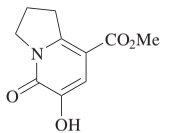
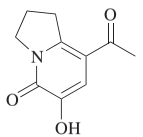
$Rh_2(OAc)_4$



Solvent	Temp		
C_6H_6	reflux	(86)	154, 159
—	—	(86)	158

$Rh_2(OAc)_4$, C_6H_6, reflux



(52)

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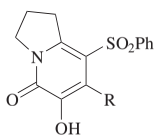
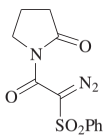
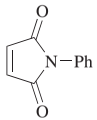
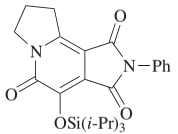
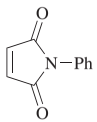
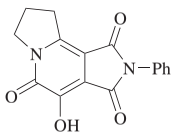
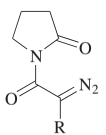
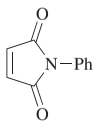
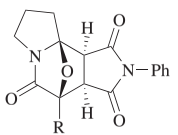
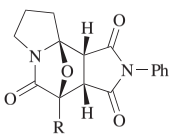
$Rh_2(OAc)_4$



R	Solvent	Temp		
H	C_6H_6	reflux	(68)	154, 159
H	—	—	(85)	158
Me	C_6H_6	reflux	(51)	154, 159

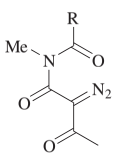
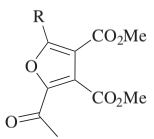
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

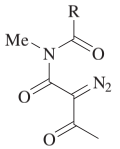
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		1. $Rh_2(OAc)_4$, C_6H_6, reflux 2. $(i\text{-}Pr)_3SiCl$, Et_3N, CH_2Cl_2, 0°	 (87)	154
		$Rh_2(OAc)_4$, C_6H_6, reflux	 (95)	159
C_{6-7} 		Catalyst, C_6H_6, 80°	 + 	

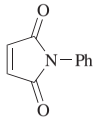
I **II**

R	Catalyst	I + II	I/II	
H	$Rh_2(OAc)_4$	(80)	70:30	153
H	$Rh_2(pfbm)_4$	(—)	79:21	167
EtO_2C	$Rh_2(pfbm)_4$	(93)	85:15	167

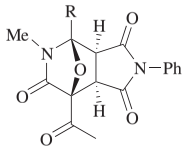
		$Rh_2(OAc)_4$, C_6H_6, 80°		R Me (82) Et (86)	184, 230

C_{6-17}





$Rh_2(OAc)_4$, C_6H_6, 80°



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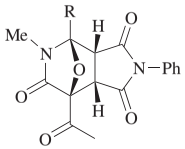
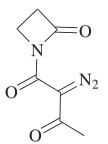
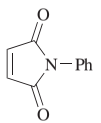


I **II**

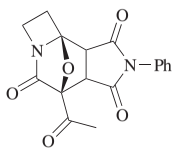
R	**I + II**	**I/II**	
Me	(76)	2.6:1	184
Et	(65)	2:1	184
2-thienyl$(CH_2)_3$	(92)	2:1	133
2-thienyl$(CH_2)_4$	(78)	—	133
1-indolyl$(CH_2)_2$	(70)	—	133
1-indolyl$(CH_2)_3$	(65)	—	133
1-indolyl$(CH_2)_4$	(80)	5:3	133
2-(1-methylindolyl)$(CH_2)_4$	(77)	—	133
2-(1-phenylsulfonylindolyl)$(CH_2)_4$	(62)	—	133

C_7

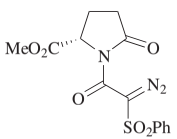




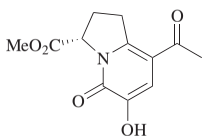
$Rh_2(OAc)_4$, C_6H_6, 80°



(61) 184, 230



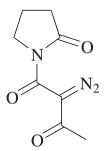
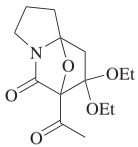
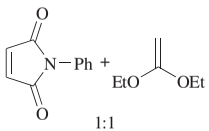
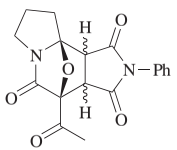
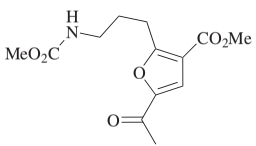
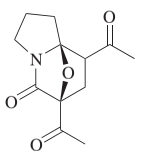
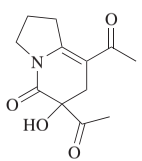
$Rh_2(OAc)_4$, C_6H_6, 80°



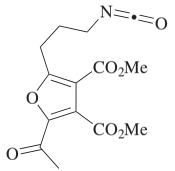
(86) 154

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		$Rh_2(OAc)_4$, C_6H_6, 80°	 (92)	153
	 1:1	$Rh_2(OAc)_4$, C_6H_6, 80°	 (79) *endo*/*exo* = 1.2:1	153
		1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. MeOH, rt	 (69)	153
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (27) +  (44)	153

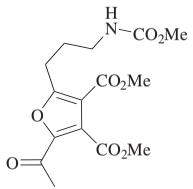
$Rh_2(OAc)_4$, C_6H_6, 80°



(85)

184, 230

1. $Rh_2(OAc)_4$, C_6H_6, 95°
2. MeOH, TsOH, rt



(90)

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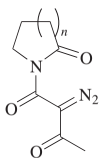
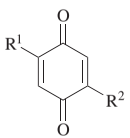
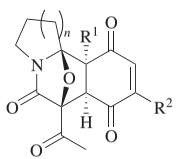
$C_{8–9}$





$Rh_2(OAc)_4$, C_6H_6, 80°



n	R^1	R^2	
1	H	H	(35)
1	Me	Me	(47)
1	H	Ph	(56)
2	H	H	(30)
2	Me	Me	(42)
2	H	Ph	(41)

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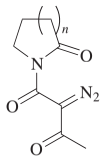
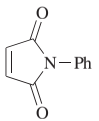
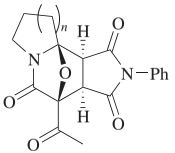
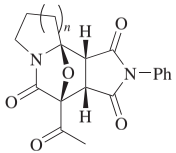
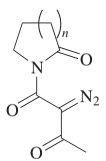
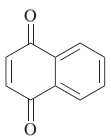
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

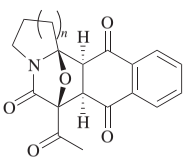
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{8–10}$ 		Catalyst, C_6H_6, 80°	 **I** +  **II**	

n	Catalyst	I + II	I/II	Refs.
1	$Rh_2(OAc)_4$	(78)	55:45	184, 230
1	$Rh_2(pfbm)_4$	(—)	65:35	167
2	$Rh_2(OAc)_4$	(85)	16:1	184, 230
3	$Rh_2(OAc)_4$	(75)	1.2:1	184, 230

$C_{8–9}$ 

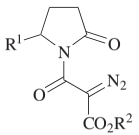


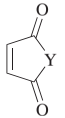
$Rh_2(OAc)_4$, C_6H_6, 80°



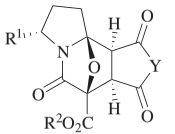
n		Refs.
1	(46)	330
2	(45)	

C_8





$Rh_2(pfbm)_4$, C_6H_6, 80°



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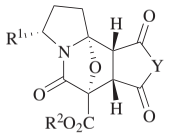

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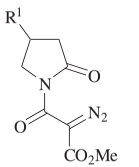
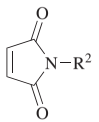
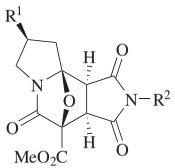
I **II**

R^1	R^2	Y	**I**	**II**	**I/II**
Me	Et	PhN	(50)	(36)	58:42
EtO_2C	Et	PhN	(71)	(14)	83:17
$CH_2{=}CHCH_2O_2C$	Et	PhN	(64)	(11)	85:15
t-BuO_2C	Et	MeN	(74)	(—)	90:10
t-BuO_2C	Et	PhN	(76)	(8)	90:10
t-BuO_2C	Et	O	(79)	(—)	90:10
BnO_2C	Me	PhN	(79)	(12)	87:13

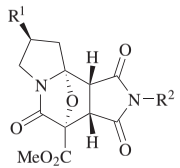




$Rh_2(pfbm)_4$, C_6H_6, 80°



+



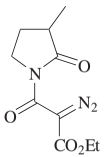
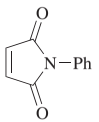
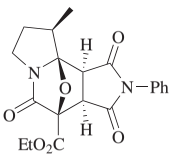
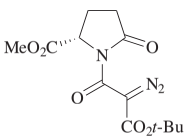
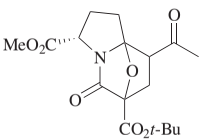
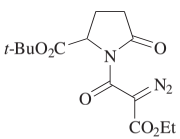
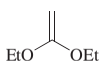
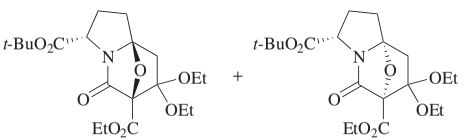
167

I **II**

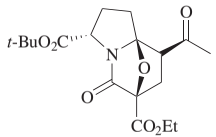
R^1	R^2	**I + II**	**I/II**
Me	Me	(91)	68:32
Me	Ph	(88)	64:36
MeO_2C	Me	(93)	45:55

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

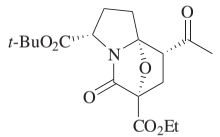
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		$Rh_2(pfbm)_4$, C_6H_6, 80°	 (86)	167
		$Rh_2(OAc)_4$, C_6H_6, 90°	 (—)	168
		$Rh_2(pfbm)_4$, C_6H_6, 80°	 **I** **I** + **II** (80), **I**/**II** = 65:35 **II**	167

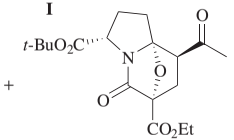
$Rh_2(pfbm)_4$, C_6H_6, 80°



I



II

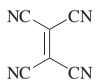


III

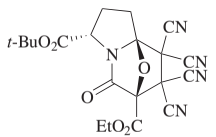
I + **II** + **III** (82)

I/II/III = 51:21:28

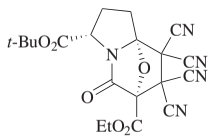
167



$Rh_2(pfbm)_4$, C_6H_6, 80°



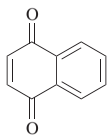
I (74)



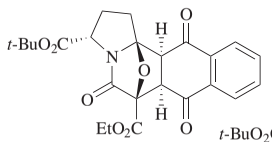
II (–)

I/II = 77:23

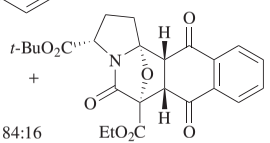
167



$Rh_2(pfbm)_4$, C_6H_6, 80°



I



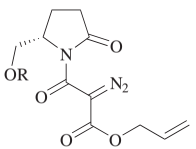
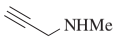
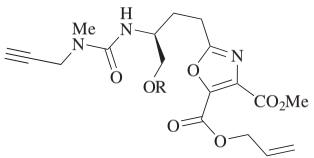
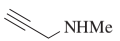
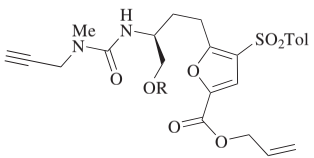
II

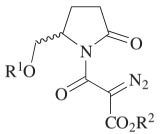
I + **II** (80), **I/II** = 84:16

167

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

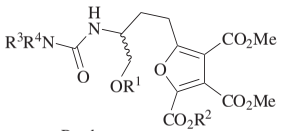
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8  R = TIPS		1. $Rh_2(oct)_4$, C_6H_6, 80° 2.  , rt	 (50)	183
		1. $Rh_2(oct)_4$, C_6H_6, 80° 2.  , rt	 (76)	183



R^1 = TIPS

1. $Rh_2(oct)_4$, C_6H_6, 80°
2. R^3R^4NH, rt



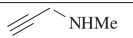
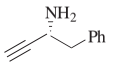
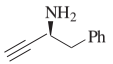
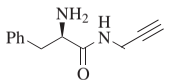
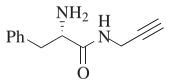
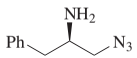
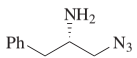
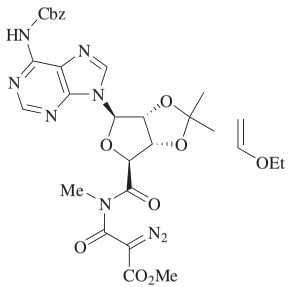
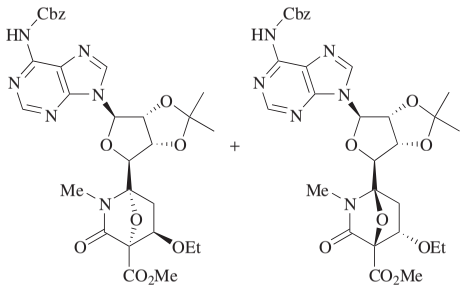
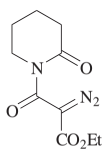
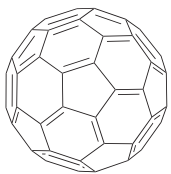
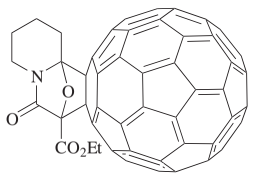
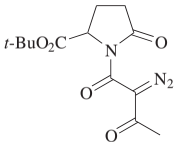
R^2	Substrate	R^3R^4NH	Product	
CH_2=$CHCH_2$	(*S*)		(*S*)	(66)
CH_2=$CHCH_2$	(*S*)		(*S*)	(79)
CH_2=$CHCH_2$	(*R*)		(*R*)	(69)
CH_2=$CHCH_2$	(*S*)		(*S*)	(69)
CH_2=$CHCH_2$	(*R*)		(*R*)	(67)
CH_2=$CHCH_2$	(*S*)		(*S*)	(82)
CH_2=$CHCH_2$	(*R*)		(*R*)	(66)
CH_2=$CHCH_2$	(*S*)		(*S*)	(73)
CH_2=$CHCH_2$	(*R*)		(*R*)	(72)
CH_2=$CHCH_2$	(*S*)		(*S*)	(54)
CH_2=$CHCH_2$	(*S*)		(*S*)	(55)
CH≡CCH_2	(*S*)		(*S*)	(67)

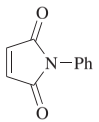
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

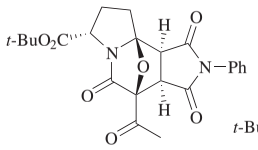
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		$Rh_2(pfbm)_4$, C_6H_5Cl, 130°, 4 Å MS	 **I** **I** + **II** (37), **I/II** = 1:1 **II**	152
		$Rh_2(pfb)_4$, 1,2-$Cl_2C_6H_4$, 90°	 (52)	144

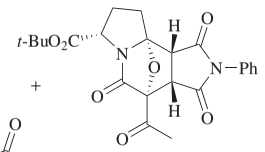
C_9

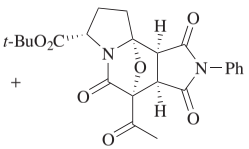




$Rh_2(pfbm)_4$, C_6H_6, 80°







I + **II** + **III** (95)

I/**II**/**III** = 81:11:8

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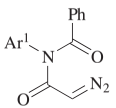
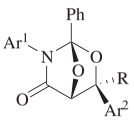


$Cu(acac)_2$, C_6H_6, 80°



R	Ar^1	Ar^2	
H	Ph	4-ClC_6H_4	(65)
H	Ph	$4\text{-O}_2NC_6H_4$	(59)
H	4-ClC_6H_4	4-ClC_6H_4	(34)
H	4-ClC_6H_4	$4\text{-O}_2NC_6H_4$	(55)
Me	Ph	$4\text{-O}_2NC_6H_4$	(31)
Me	4-ClC_6H_4	$4\text{-O}_2NC_6H_4$	(57)

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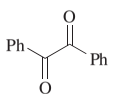
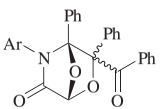


$Cu(acac)_2$, C_6H_6, 80°



Ar	
Ph	(67)
4-ClC_6H_4	(79)

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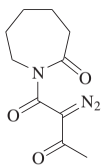
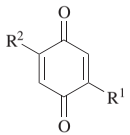
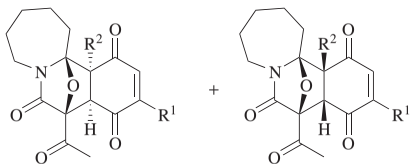
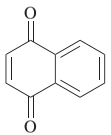
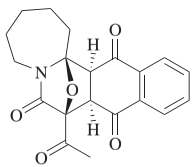
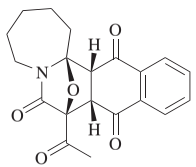
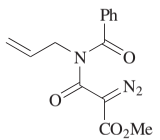
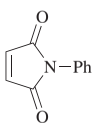
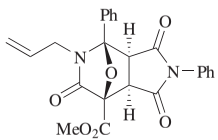
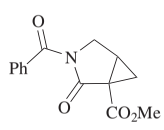
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

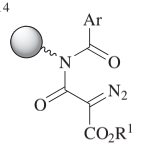
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 		$Rh_2(OAc)_4$, C_6H_6, 80°	 **I** + **II**	330
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (55) +  (30)	330
		Catalyst	 **I** +  **II**	210

Catalyst	Solvent	Temp	I	II
$Rh_2(OAc)_4$	C_6H_6	80°	(60)	(40)
$Rh_2(tfa)_4$	—	—	(100)	(—)

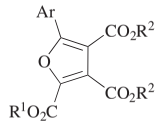
R^1	R^2	I	II
H	H	(38)	(32)
Me	Me	(45)	(40)
Ph	H	(39)	(33)

C_{10-14}



= Tentagel^{TM}–NH_2 resin

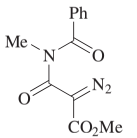
$Rh_2(OAc)_4$, C_6H_6, 80°



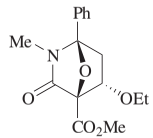
232

Ar	R^1	R^2	
4-$MeOC_6H_4$	Me	Me or Et	(—)
4-$MeOC_6H_4$	Et	Me	(—)
4-$MeOC_6H_4$	Et	Et	(60)
3,4,5-$(MeO)_3C_6H_2$	Me or Et	Me or Et	(—)
4-*t*-BuC_6H_4	Me or Et	Me or Et	(—)

C_{10}



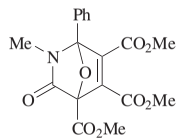
$Rh_2(pfbm)_4$, C_6H_6, 80°



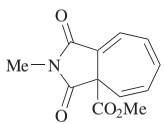
(>98)

94

Catalyst



+

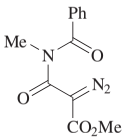
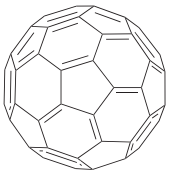
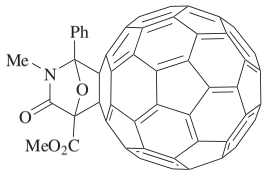
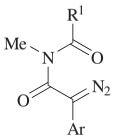
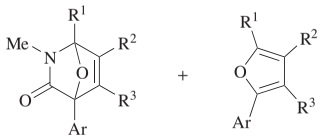


I **II**

Catalyst	**I + II**	**I/II**	
$Rh_2(OAc)_4$	(—)	50:50	233, 234
$Rh_2(tfa)_4$	(—)	98:2	234
$Rh_2(pfbm)_4$	(—)	100:0	233, 234

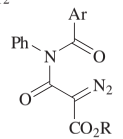
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

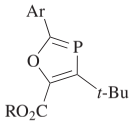
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 		$Rh_2(pfb)_4$, 1,2-$Cl_2C_6H_4$, 90°	 (40)	144
C_{10-15}  Ar = 4-$O_2NC_6H_4$		$Cu(acac)_2$	 **I** + **II**	331

R^1	R^2	R^3	Solvent	Temp (°)	**I**	**II**
Me	MeO_2C	MeO_2C	C_6H_6	80	(81)	(16)
Ph	MeO_2C	H	C_6H_6	30[b]	(82)	(1)
Ph	MeO_2C	H	C_6H_6	80	(35)	(44)
Ph	MeO_2C	MeO_2C	C_6H_6	30[b]	(92)	(5)
Ph	MeO_2C	MeO_2C	C_6H_6	80	(42)	(54)
Ph	MeO_2C	MeO_2C	xylene	100	(—)	(83)
Ph	Ph	Ph	xylene	120	(—)	(27)
Ph	Bz	Bz	C_6H_6	30[b]	(69)	(—)
Ph	Bz	Bz	xylene	120	(—)	(88)

C_{10-12}

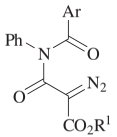


$Rh_2(OAc)_4$, toluene, argon (5 bar), 120°

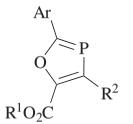


Ar	R		
Ph	Me	(48)	
4-$MeOC_6H_4$	Me	(36)	200
4-$MeOC_6H_4$	Et	(45)	
4-MeC_6H_4	Et	(39)	
4-EtC_6H_4	Me	(38)	

C_{10-14}

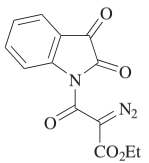


1. $Rh_2(OAc)_4$, toluene, 100°
2. Dipolarophile, argon (5 bar), THF, 120°

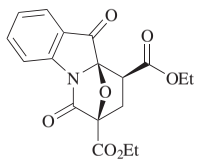


Ar	R^1	R^2		
Ph	Et	*t*-Bu	(39)	
Ph	Et	*t*-C_5H_{11}	(37)	200
4-$MeOC_6H_4$	Et	*t*-Bu	(34)	
Mes	Et	*t*-Bu	(35)	
1-naphthyl	Me	*t*-Bu	(37)	
2-naphthyl	Me	*t*-Bu	(38)	

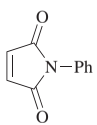
C_{11}



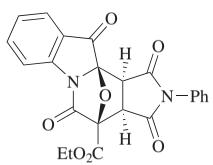
$Rh_2(OAc)_4$, C_6H_6, 80°



(55) 345



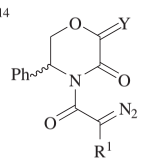
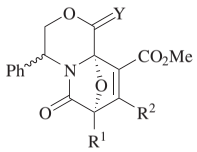
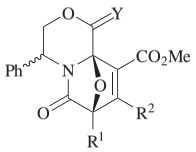
$Rh_2(OAc)_4$, C_6H_6, 80°



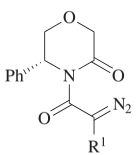
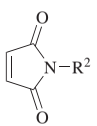
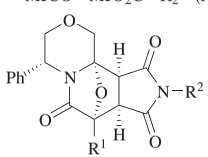
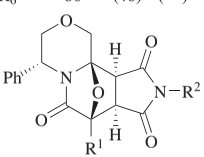
(74) 345

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{12–14}$ 		$Rh_2(OAc)_4$	 +  **I** **II**	

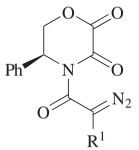
R^1	R^2	Y		Solvent	Temp (°)	I	II	
H	MeO_2C	H_2	(*R*)	CH_2Cl_2	rt	(39)	(26)	332
H	MeO_2C	O	(*S*)	CH_2Cl_2	rt	(6)	(54)	89
EtO_2C	H	H_2	(*R*)	C_6H_6	80	(65)	(—)	332
EtO_2C	MeO_2C	H_2	(*R*)	C_6H_6	80	(65)	(—)	332
EtO_2C	MeO_2C	O	(*R*)	C_6H_6	80	(53)	(12)	89
MeCO	H	H_2	(*R*)	C_6H_6	80	(70)	(—)	332
MeCO	MeO_2C	H_2	(*R*)	C_6H_6	80	(46)	(—)	332

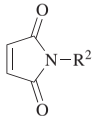
  $Rh_2(OAc)_4$  +  332

I **II**

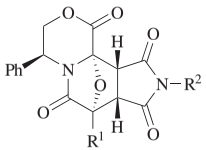
R^1	R^2	Solvent	Temp (°)	I	II
H	Me	CH_2Cl_2	rt	(52)	(8)
H	Ph	CH_2Cl_2	rt	(37)	(25)
EtO_2C	Me	C_6H_6	80	(65)	(15)
EtO_2C	Ph	C_6H_6	80	(54)	(20)
MeCO	Me	C_6H_8	80	(70)	(19)
MeCO	Ph	C_6H_6	80	(59)	(21)

C_{12-13}

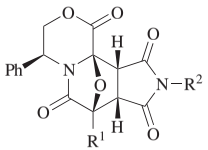




$Rh_2(OAc)_4$



I

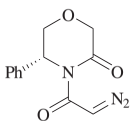


II

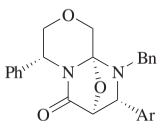
89

R^1	R^2	Solvent	Temp (°)	**I**	**II**
H	Ph	CH_2Cl_2	rt	(18)	(32)
EtO_2C	Me	C_6H_6	80	(24)	(56)
EtO_2C	Ph	C_6H_6	80	(20)	(54)

C_{12}



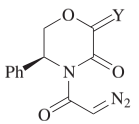
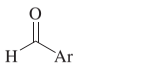
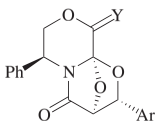
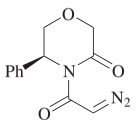
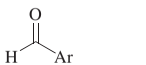
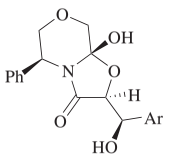
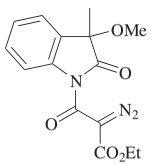
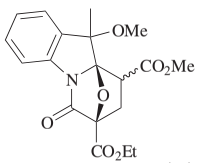
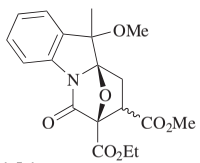
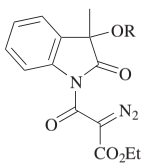
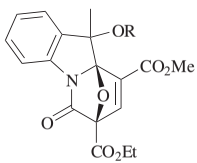
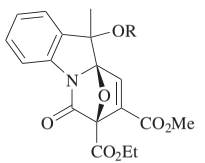
$Rh_2(OAc)_4$, 3 Å MS

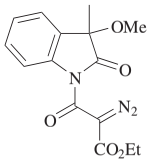


Ar	Solvent	Temp		
Ph	$MeNO_2$	rt	(70)	
4-ClC_6H_4	$MeNO_2$	rt	(30)	92
4-$Me_2NC_6H_4$	$MeNO_2$	rt	(21)	
4-$O_2NC_6H_4$	$MeNO_2$	rt	(47)	
4-$MeOC_6H_4$	CH_2Cl_2	−78°	(0)	
4-$MeOC_6H_4$	CH_2Cl_2	0°	(7)	
4-$MeOC_6H_4$	CH_2Cl_2	rt	(12)	
4-$MeOC_6H_4$	CH_2Cl_2	reflux	(10)	
4-$MeOC_6H_4$	$CHCl_3$	rt	(2)	
4-$MeOC_6H_4$	THF	rt	(3)	
4-$MeOC_6H_4$	THF	reflux	(0)	
4-$MeOC_6H_4$	EtOAc	rt	(0)	
4-$MeOC_6H_4$	MeOH	rt	(0)	
4-$MeOC_6H_4$	$MeNO_2$	rt	(43)	

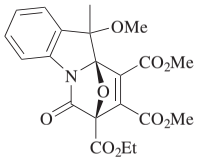
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
	 Ar = 4-$O_2NC_6H_4$	$Rh_2(OAc)_4$, CH_2Cl_2, rt	 Y: H_2 (21); O (45)	333
	 Ar = 4-$MeOC_6H_4$	1. $Rh_2(OAc)_4$, CH_2Cl_2, rt 2. H^+, H_2O	 (16)	333
		$Rh_2(OAc)_4$, C_6H_6, 80°	 +  (—) dr 4.5:2:1.5:1	164
		$Rh_2(OAc)_4$, C_6H_6, 80°	 +  **I** **II**	164
			R: Me (70) I/II 1:1; TBS (70) I/II 1:3	



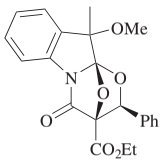

$Rh_2(OAc)_4$, C_6H_6, 80°



(98)

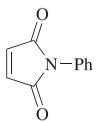
164

$Rh_2(OAc)_4$, C_6H_6, 80°

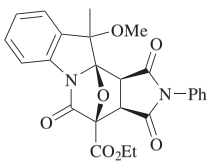


(98)

164



$Rh_2(OAc)_4$, C_6H_6, 80°



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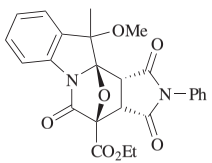
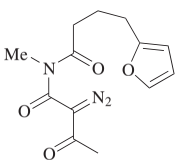
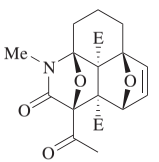


164

I **I** + **II** (95), **I**/**II** = 3:2 **II**




$Rh_2(OAc)_4$, C_6H_6, 80°



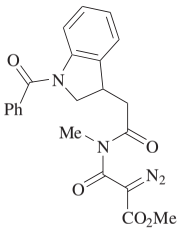
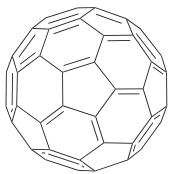
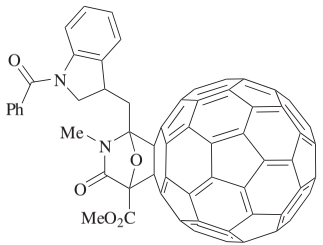
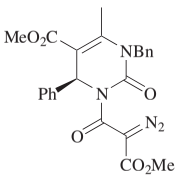
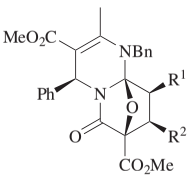
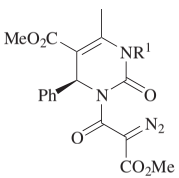
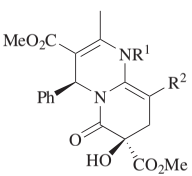
(56)

E = CO_2Me

61, 133

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 		$Rh_2(pfb)_4$, 1,2-$Cl_2C_6H_4$, 90°	 (48) dr 2.1:1	144
C_{15} 		$Rh_2(OAc)_4$, C_6H_6, 80°		75
		1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. TsOH, CH_2Cl_2		75

R^1	R^2	
NC	H	(90)
MeO_2C	MeO_2C	(90)

R^1	R^2	
Et	MeOC	(92)
Bn	NC	(95)
Bn	MeO_2C	(87)
Bn	MeCO	(90)

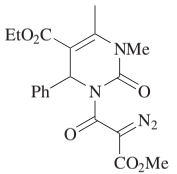
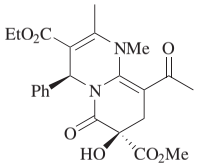
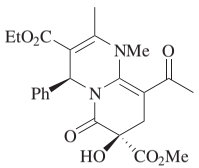
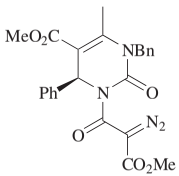
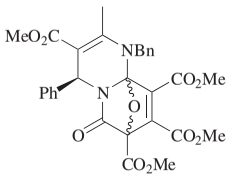
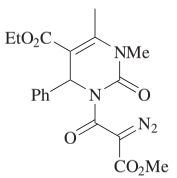
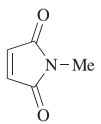
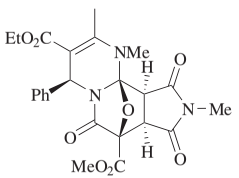
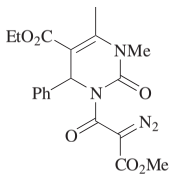
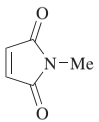
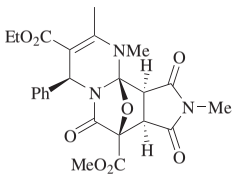
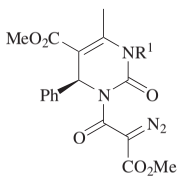
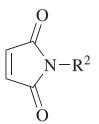
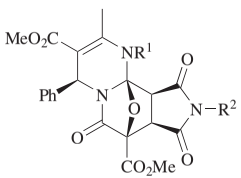
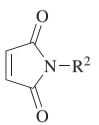
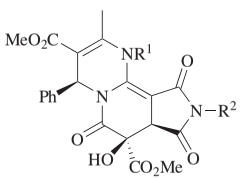
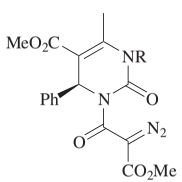
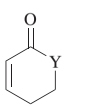
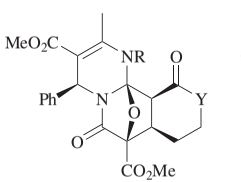
		$Rh_2(OAc)_4$, C_6H_6, 80°		(71)	63
		1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. Dipolarophile, CH_2Cl_2, rt		(71)	63
		$Rh_2(OAc)_4$, C_6H_6, 80°		(90) dr 2:1	75
		$Rh_2(OAc)_4$, C_6H_6, 80°		(80)	63

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

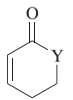
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 		1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. Dipolarophile, CH_2Cl_2, rt	 (72)	63
		$Rh_2(OAc)_4$, C_6H_6, 80°		75
		1. $Rh_2(OAc)_4$, C_6H_6, 80° 2. TsOH, CH_2Cl_2		75
		$Rh_2(OAc)_4$, C_6H_6, 80°		75

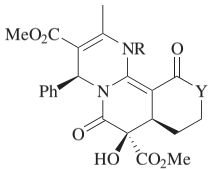
R^1	R^2	
Et	Me	(93)
Bn	Me	(91)
Et	Ph	(92)
Bn	Ph	(88)

R^1	R^2	
Et	Me	(74)
Bn	Me	(72)
Et	Ph	(73)
Bn	Ph	(72)

R	Y	
Et	O	(75)
Bn	O	(86)
Et	CH_2	(83)
Bn	CH_2	(85)

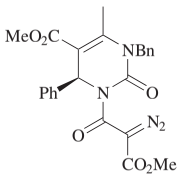


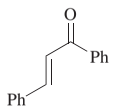
1. $Rh_2(OAc)_4$, C_6H_6, 80°
2. TsOH, CH_2Cl_2



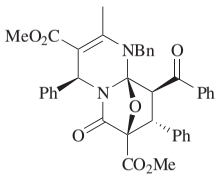
R	Y	
Et	CH_2	(76)
Bn	CH_2	(80)
Bn	O	(73)

75



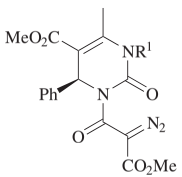


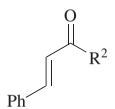
$Rh_2(OAc)_4$, C_6H_6, reflux



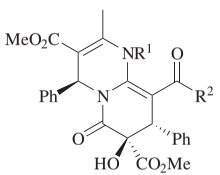
(87)

75



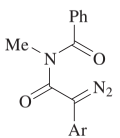


1. $Rh_2(OAc)_4$, C_6H_6, 80°
2. TsOH, CH_2Cl_2



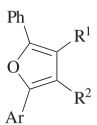
R^1	R^2	
Et	Me	(65)
Et	Ph	(85)
Bn	Me	(84)
Bn	Ph	(95)

75



Ar = 4-$O_2NC_6H_4$

$Cu(acac)_2$



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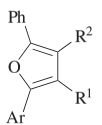

I **II**

R^1	R^2	Solvent	Temp (°)	**I**	**II**
H	*n*-Bu	xylene	100	(75)	(—)
H	Ph	C_6H_6	80	(82)	(3)
Me	MeO_2C	C_6H_6	80	(81)	(—)
Ph	MeO_2C	C_6H_6	80	(91)	(—)

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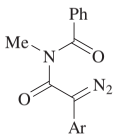
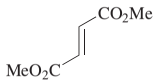
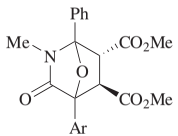
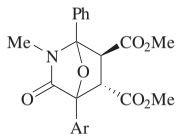
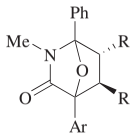
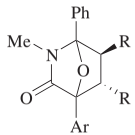
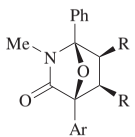
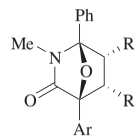
TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

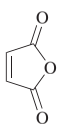
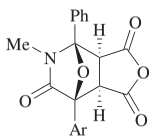
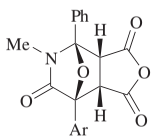
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}  Ar = 4-$O_2NC_6H_4$		1. Cu(acac)$_2$, C_6H_6, 80° 2. Dipolarophile, C_6H_6, 80°	 (85) +  (—)	59, 334
		Cu(acac)$_2$, C_6H_6, 80°	 **I** +  **II**	59

R	I	II
Ph	(29)	(17)
Bz	(23)	(77)

	Cu(acac)$_2$, C_6H_6, 80°	 **I** +  **II**	59

R	I	II
MeO_2C	61	(34)
Ph	(59)	(—)

	Cu(acac)$_2$, C_6H_6, 80°	 **I** +  **II**	59

I + **II** (84), **I**/**II** = 7:2
determined on derivative

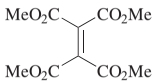
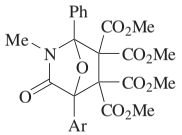
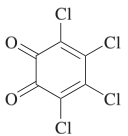
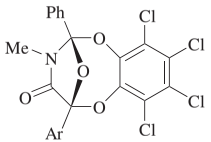
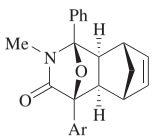
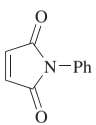
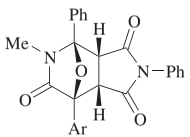
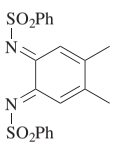
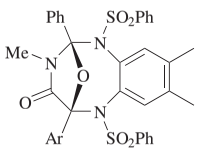
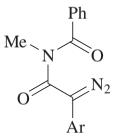
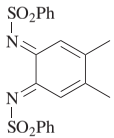
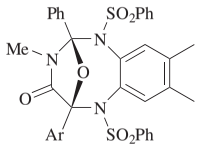
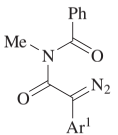
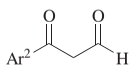
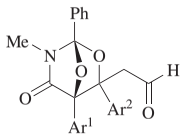
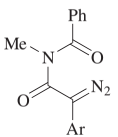
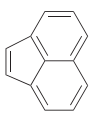
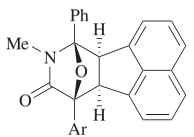
	$Cu(acac)_2$, C_6H_6, 80°		(31)	59
	1. $Cu(acac)_2$, C_6H_6, 80° 2. Dipolarophile, CH_2Cl_2, rt		(93)	335
	$Cu(acac)_2$, C_6H_6, 80°		(55)	59
	$Cu(acac)_2$, C_6H_6, 80°		(87)	59
	1. $Cu(acac)_2$, C_6H_6, 80° 2. Dipolarophile, CH_2Cl_2, rt		(93)	335

TABLE 17. INTERMOLECULAR CYCLOADDITIONS OF 5-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

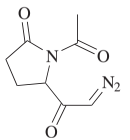
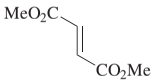
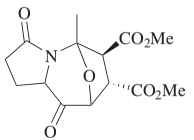
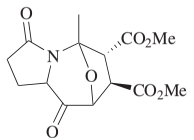
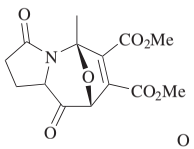
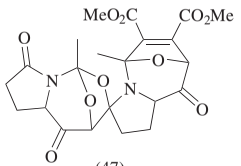
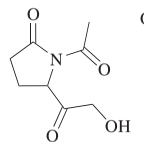
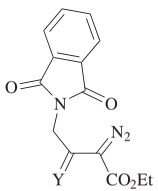
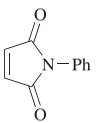
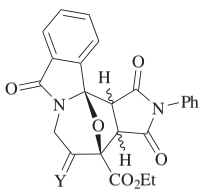
B. ISOMÜNCHNONES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}				
 Ar = 4-$O_2NC_6H_4$		1. Cu(acac)$_2$, C_6H_6, 80° 2. Dipolarophile, CH_2Cl_2, rt	 (93)	335
 Ar^1 = 4-$O_2NC_6H_4$	 Ar^2 = 4-ClC_6H_4	$Cu(acac)_2$, C_6H_6, 80°	 (57)	187
 Ar = 4-$O_2NC_6H_4$		$Cu(acac)_2$, C_6H_6, 80°	 (100)	59

[a] The hydroxylamine was generated from the hydrochloride with triethylamine.

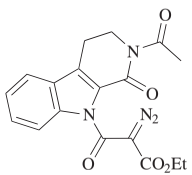
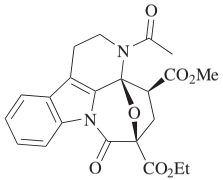
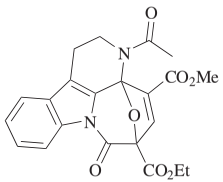
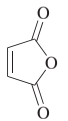
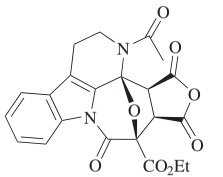
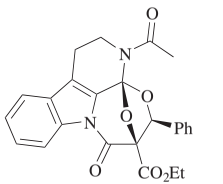
[b] The isolated isomünchnone was treated with the dipolarophile.

TABLE 18. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM IMIDES

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		$Rh_2(OAc)_4$, C_6H_6, rt	 (30) +  (12)	223
		$Rh_2(OAc)_4$, $CHCl_3$, rt	 (36) +  (47) +  (8)	223
C_{12} 		$Rh_2(oct)_4$, C_6H_6		230

Y	Temp	
H_2	rt	(92)
O	80°	(87)

TABLE 18. INTERMOLECULAR CYCLOADDITIONS OF 6-MEMBERED-RING CARBONYL YLIDES FROM IMIDES (*Continued*)

Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 		$Rh_2(OAc)_4$, C_6H_6, 80°	 (77)[a]	164, 231
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (78)	164, 231
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (75)[a]	164, 231
		$Rh_2(OAc)_4$, C_6H_6, 80°	 (85)[a]	164, 231

[a] The initial stereochemical assignment of the cycloadduct was incorrect, and data was corrected (ref.231).

TABLE 19. INTERMOLECULAR CYCLOADDITIONS OF 7-MEMBERED-RING CARBONYL YLIDES FROM IMIDES

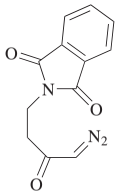
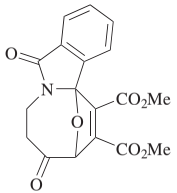
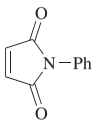
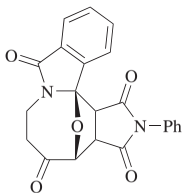
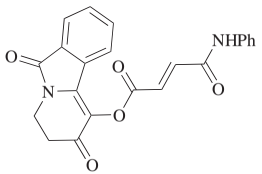
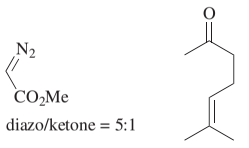
Diazo Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (63)	111
		$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (45) +  (26)	111

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES

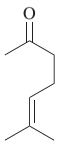
Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.

See Charts **1** *and* **2** *for the structures of catalysts and ligands represented by* ***bold*** *numbers in the Tables.*

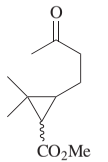
C_2



diazo/ketone = 5:1

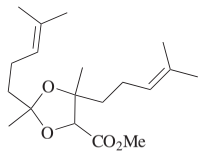


Cu-bronze catalyst, 105°



(41) *cis/trans* 45:55

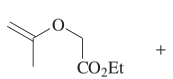
+



(30) *cis/trans* 41:55

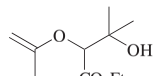
336

Cu, 90°, 30 psi



I (24)

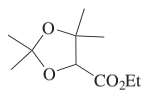
+



II

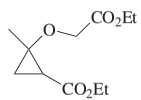
337

+



III

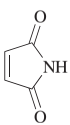
+

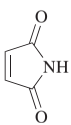


IV (23)

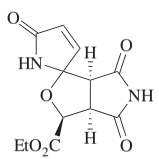
II + **III** (9)

+ 3:1 adduct **V** (4)



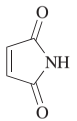


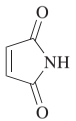
$Rh_2(OAc)_4$, CH_2Cl_2, rt



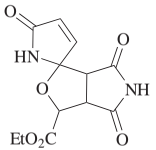
(87)

247



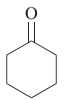


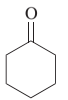
$Rh_2(OAc)_4$, CH_2Cl_2, rt



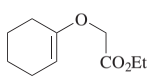
(87)
mixture of 3 diastereomers

248



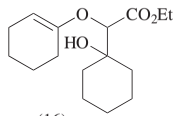


Cu, 90°



(43) (crude)

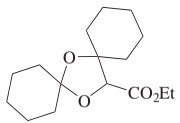
+



(16)

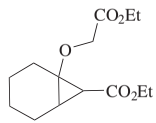
337

+



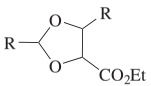
(4) (estimate)

+



(1) (estimate)

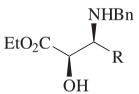
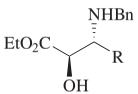
160–170°



R	
n-C_6H_{13}	(—)
Ph	(40)

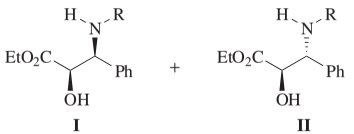
235

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
 addition time 1 h			1. Catalyst, 4 Å MS pwd., solvent, temp 2. TsOH, MeOH, H_2O, rt	 **I** +  **II**	

R	Catalyst	Solvent	Temp	I	I/II	er I	
EtO_2C	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(64)	83:17	—	195, 197
2-furyl[a]	$Rh_2(OAc)_4$	CH_2Cl_2	0°	(75)	92:8	—	195, 197
Ph	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(82)	93:7	—	195, 197
Ph	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(13)	88:12	—	197
Ph	$Rh_2(OAc)_4$, $Cu(OTf)_2$ (5 mol %)	CH_2Cl_2	rt	(67)	67:33	—	197
Ph	$Rh_2(OAc)_4$, $Yb(OTf)_3$ (5 mol %)	CH_2Cl_2	rt	(70)	64:36	—	197
Ph	**10b**	CH_2Cl_2	rt	(62)	94:6	62.0:38.0	197
Ph	**10b**	hexane	rt	(17)	71:29	82.0:18.0	197
Ph	**10b**	Et_2O	rt	(14)	78:22	81.0:19.0	197
Ph	**9c**	CH_2Cl_2	0°	(56)	90:10	52.0:48.0	197
Ph	**14**	CH_2Cl_2	rt	(<5)	—	—	197
4-FC_6H_4	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(78)	97:3	—	195, 197
4-ClC_6H_4	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(75)	98:2	—	195, 197
4-$O_2NC_6H_4$[a]	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(61)	91:9	—	195, 197
3-$MeOC_6H_4$	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(77)	98:2	—	195, 197
4-$MeOC_6H_4$[a]	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(78)	94:6	—	195, 197
4-MeC_6H_4	$Rh_2(OAc)_4$	CH_2Cl_2	rt	(87)	97:3	—	195, 197
2-naphthyl[a]	$Rh_2(OAc)_4$	CH_2Cl_2	0°	(83)	98:2	—	195, 197

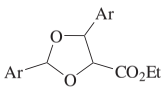
1. $Rh_2(OAc)_4$, 4 Å MS pwd., CH_2Cl_2, temp
2. TsOH, $MeOH/H_2O$ (95:5), rt



I + **II**

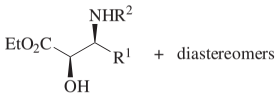
197

R	Ar	Temp	I	I/II	I/III	I + II + III	(I + II)/III
Bn	4-$O_2NC_6H_4$	rt	(47)	85:15	60:40	(—)	(—)
Bn	4-$MeOC_6H_4$	rt	(67)	80:20	>98:2	(—)	(—)
Ts	Ph	45°	(—)	(—)	(—)	(19)	40:60

+ 

III

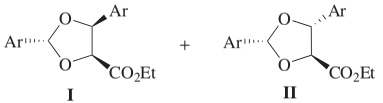
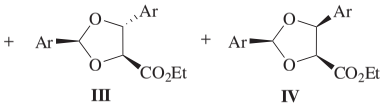
1. $Rh_2(OAc)_4$, L. A., 4 Å MS pwd., CH_2Cl_2, 0°
2. TsOH, $MeOH/H_2O$ (95:5), rt



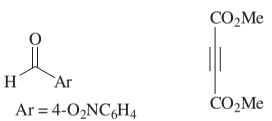
+ diastereomers

R^1	R^2	L. A.		dr	
EtO_2C[b]	(*R*)-PhMeCH	—	(58)	9.3:1.8:1:0	197
2-furyl[b]	(*R*)-PhMeCH	—	(67)	1.8:1.6:1:0	197
Ph	(*R*)-PhMeCH	—	(77)	8:1:1:0	195, 197
Ph	(*R*)-Ph($MeOCH_2$)CH	—	(—)	—	197
Ph	(*R*)-Ph($MeOCH_2$)CH	Yb(OTf)	(75)	3.6:3:1.7:1	197
Ph	(*R*)-Ph($MeOCH_2$)CH	$Zn(OTf)_3$	(93)	9.3:1.8:1:0	197
Ph		—	(—)	—	197
Ph	(*R*)-$C_{10}H_7$MeCH	—	(trace)	—	197
4-FC_6H_4	(*R*)-PhMeCH	—	(71)	4.5:1:1:0	197
4-BrC_6H_4	(*R*)-PhMeCH	—	(62)	8.4:1:1:0	197
3-$MeOC_6H_4$	(*R*)-PhMeCH	—	(87)	7.1:1:1:0	197
3-$MeOC_6H_4$[a]	(*R*)-PhMeCH	—	(82)	8.3:1:1:0	197
4-$MeOC_6H_4$	(*R*)-PhMeCH	—	(86)	5.4:1:1:0	197

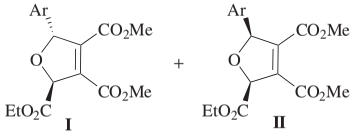
TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 			Catalyst, CH_2Cl_2	 **I** + **II**	
			Catalyst, CH_2Cl_2	 **III** + **IV**	

Ar	Catalyst	Temp	I + II + III + IV	I/II/III/IV	
Ph	$Rh_2(cap)_4$	40°	(27)	52:48:0:0	86
Ph	(*S*)-**6**	40°	(39)	49:45:0:6	86
4-FC_6H_4	$Cu[MeCN)_4PF_6$	reflux	(60)	31:28:0:41	189
4-FC_6H_4	$Rh_2(OAc)_4$	reflux	(68)	44:52:0:4	189
4-ClC_6H_4	$Cu[MeCN)_4PF_6$	reflux	(57)	24:34:0:42	189
4-ClC_6H_4	$Rh_2(OAc)_4$	reflux	(48)	45:43:0:12	189
4-ClC_6H_4	$Rh_2(cap)_4$	reflux	(18)	38:47:0:15	189
4-$O_2NC_6H_4$	$Cu[MeCN)_4PF_6$	40°	(39)	11:9:10:70	86, 189
4-$O_2NC_6H_4$	$Rh_2(OAc)_4$	40°	(37)	21:22:3:54	86, 189
4-$O_2NC_6H_4$	$Rh_2(pfb)_4$	40°	(41)	28:20:7:45	86
4-$O_2NC_6H_4$	$Rh_2(cap)_4$	40°	(35)	43:41:0:16	86, 189
4-$MeOC_6H_4$	$Cu[MeCN)_4PF_6$	reflux	(38)	37:40:4:19	189
4-$MeOC_6H_4$	$Rh_2(OAc)_4$	40°	(15)	52:48:0:0	86
4-$MeOC_6H_4$	$Rh_2(cap)_4$	40°	(52)	52:48:0:0	86
4-$MeOC_6H_4$	(*S*)-**6**	40°	(77)	52:48:0:0	86
4-$CF_3C_6H_4$	$Cu[MeCN)_4PF_6$	reflux	(72)	22:24:6:48	189
4-$CF_3C_6H_4$	$Rh_2(OAc)_4$	reflux	(93)	28:43:5:24	189
4-$CF_3C_6H_4$	$Rh_2(cap)_4$	reflux	(50)	33:38:3:26	189

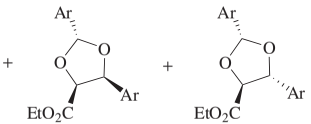


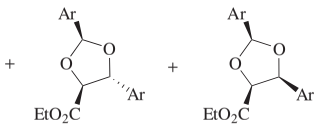
$Rh_2(OAc)_4$, CH_2Cl_2, rt



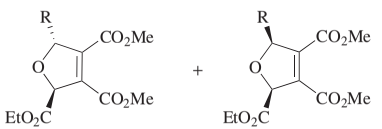
86

Diazo/Aldehyde/DMAD	I + II + III	I/II/III	(I + II)/III	III (a/b/c/d)
1:3:3	(30)	43:30:27	—	9:9:trace:82
1:6:3	(31)	—	55:45	11:11:trace:78





$Rh_2(OAc)_4$, CH_2Cl_2, rt



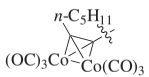
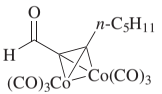
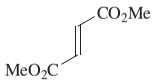
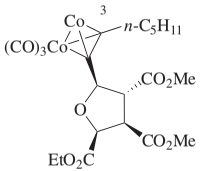
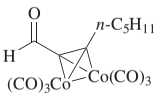
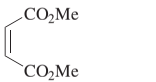
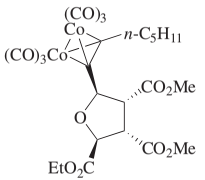
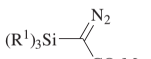
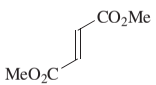
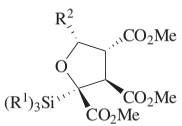
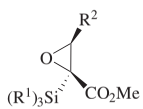
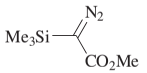
R	I + II	I/II	
n-C_5H_{11}–C≡C–	(9)	3:1	242
	(68)	<1:20	242
4-$MeOC_6H_4$	(51)	**I** only	86

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

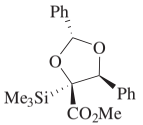
Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
			$Rh_2(OAc)_4$, CH_2Cl_2, 40°	 (50) dr 6:1	242
			$Rh_2(OAc)_4$, CH_2Cl_2, rt	 (50) dr >20:1	242
			Catalyst	 + 	243

I **II**

R^1	R^2	Catalyst	Solvent	Temp (°)	I	II
Me	Me	$Rh_2(pfb)_4$	CH_2Cl_2	rt	(43)	(—)
Me	(*E*)-MeCH=CH	$Rh_2(pfb)_4$	CH_2Cl_2	22	(44)	(—)
Me	Ph	$Rh_2(pfb)_4$	CH_2Cl_2	22	(41)	(—)
Me	Ph	$[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$	C_6H_6	80	(54)	(—)
Me	Ph	CuOTf	CH_2Cl_2	22	(12)	(38)
Et	Ph	$Rh_2(pfb)_4$	CH_2Cl_2	22	(46)	(—)



Catalyst



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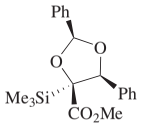
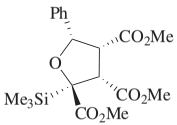


243

I **II**

Catalyst	Solvent	Temp	I + II	I/II
$Rh_2(pfb)_4$	CH_2Cl_2	rt	(23)	70:30
$[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$	C_6H_6	80°	(23)	**I** only

Catalyst, CH_2Cl_2, 22°



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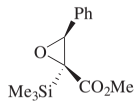
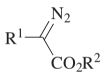


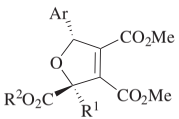
243

I **II**

Catalyst	I	II
$Rh_2(pfb)_4$	(49)	(—)
CuOTf	(16)	(38)

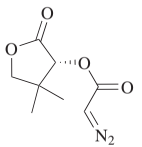
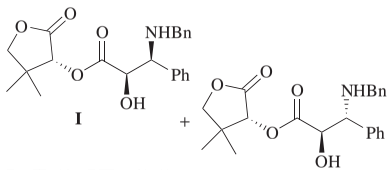
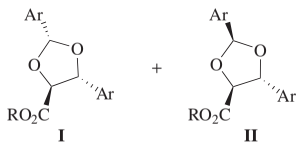
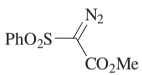
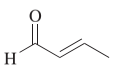
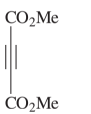
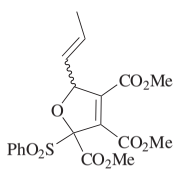


Catalyst, CH_2Cl_2



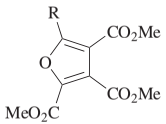
R^1	R^2	Ar	Catalyst	Temp		
H	2,6-(*t*-Bu)$_2$-4-MeC_6H_2	4-MeOC_6H_4	$Rh_2(OAc)_4$	rt	(67)	86
Me_3Si	Me	Ph	$Rh_2(pfb)_4$	22°	(62)	243

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

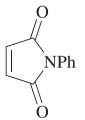
Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
			1. $Rh_2(OAc)_4$, 4 Å MS pwd., CH_2Cl_2, 0° 2. TsOH, MeOH/H_2O (95:5), rt	 **I** + **II** (82), **I/II** = 60:40	197
	 Ar = 4-$MeOC_6H_4$		$Rh_2(OAc)_4$, CH_2Cl_2, 40°	 **I** + **II**	86
			$Rh_2(oct)_4$, $C_2H_4Cl_2$, heat	 (27)	42

R	**I** + **II**	**I/II**
Cy_2CH	(74)	**I** only
2,6-(*t*-Bu)$_2$-4-MeC_6H_2	(59)	96:4

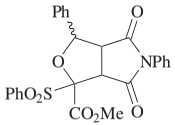
1. $Rh_2(oct)_4$, rt
2. Et_3N, 65°



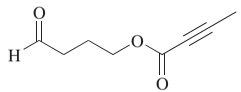
R		
	(35)	
Ph	(42)	42
4-$MeOC_6H_4$	(17)	
4-$MeO_2CC_6H_4$	(15)	



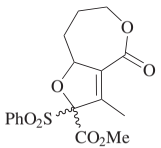
$Rh_2(oct)_4$, rt



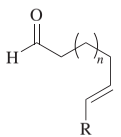
(77) 42



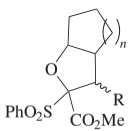
$Rh_2(oct)_4$, DCE, 80°



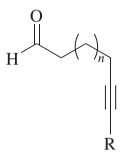
(61) 42



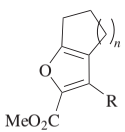
$Rh_2(oct)_4$, DCE, 65°



n	R		
1	H	(44)	42
2	Et	(28)	

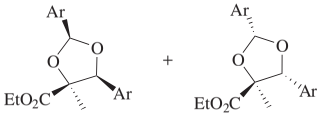
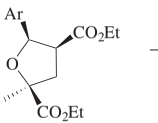


$Rh_2(oct)_4$, DCE, 65°



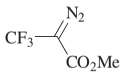
n	R		
1	H	(46)	
1	Me_3Si	(34)	42
1	MeO_2C	(42)	
1	Ph	(36)	
2	H	(65)	
3	H	(0)	

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

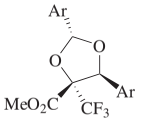
Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3					
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°	 **I** + **II**	244
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°		106

Ar	I + II	I/II
2-thienyl	(58)	94:6
Ph	(65)	>95:5
4-ClC_6H_4	(75)	>95:5
4-$O_2NC_6H_4$	(64)	94:6

Ar		dr
Ph	(59)	88:12
4-$O_2NC_6H_4$	(73)	88:12

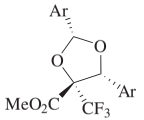


$Rh_2(OAc)_4$, CH_2Cl_2, rt



I

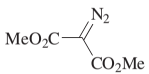
+



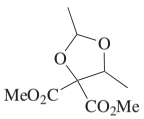
II

87

Ar	**I** + **II**	**I**/**II**
4-FC_6H_4	(89)	**I** only
2-ClC_6H_4	(91)	91:9
4-ClC_6H_4	(82)	**I** only
3-$MeOC_6H_4$	(85)	**I** only
4-$MeOC_6H_4$	(95)	**I** only
3-$PhOC_6H_4$	(94)	**I** only
2-(CHO)C_6H_4	(82)	90:10

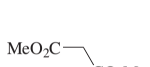


hν (λ > 340 nm)



I

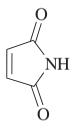
+

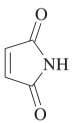


II

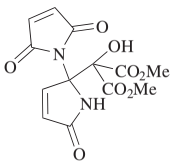
I + **II** (12), **I**/**II** = 1:1

338





$Rh_2(OAc)_4$, CH_2Cl_2, rt



(81)

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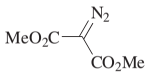
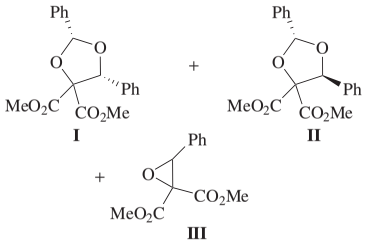
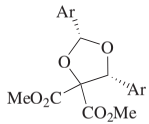
TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3					
			Catalyst		

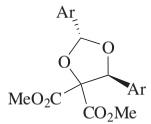
Diazo/Aldehyde	Catalyst	Solvent	Temp	I + II	I/II	III	(I + II)/III	Refs.
—	—	—	125°	(56)	58:42	(10)	—	339
—	$Rh_2(OAc)_4$	—	75°	(72)	55:45	(—)	—	339
1:1	$Rh_2(OAc)_4$	CH_2Cl_2	reflux	(23)	58:42	(30)	44:56	256
1:2	$Rh_2(OAc)_4$	CH_2Cl_2	reflux	(26)	—	(9)	75:25	256
1:5	$Rh_2(OAc)_4$	CH_2Cl_2	reflux	(18)	—	(2)	91:9	256
—	$Cu(acac)_2$	—	125°	(82)	55:45	(7)	—	339
—	CuOTf	—	rt	(87)	71:29	(—)	—	339
1:0.95	CuOTf	C_6H_5Cl	100°	(—)	—	(—)	77:23	339
1:1.9	CuOTf	C_6H_5Cl	100°	(—)	—	(—)	82:18	339
1:2.86	CuOTf	C_6H_5Cl	100°	(—)	—	(—)	89:11	339
1:4.32	CuOTf	C_6H_5Cl	100°	(—)	—	(—)	92:8	339

$Rh_2(OAc)_4$, CH_2Cl_2, reflux



I

+



II

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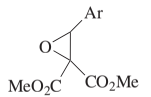
Ar	Diazo/Aldehyde	**I + II + III**	**I/II**	**(I + II)/III**
4-ClC_6H_4	1:1	(54)	62:38	57:43
4-ClC_6H_4	1:2	(28)	—	83:17
4-ClC_6H_4	1:5	(4)	—	95:5
4-$O_2NC_6H_4$	1:1	(47)	63:37	100:0
4-$MeOC_6H_4$	1:1	(62)	—	**III** only
4-$MeOC_6H_4$	1:2	(20)	—	**III** only
4-MeC_6H_4	1:1	(52)	58:42	20:80
4-MeC_6H_4	1:2	(17)	—	36:64
4-MeC_6H_4	1:5	(14)	—	51:49
4-$CF_3C_6H_4$	1:1	(50)	60:40	80:20
4-$CF_3C_6H_4$	1:2	(39)	—	100:0
4-$CF_3C_6H_4$	1:5	(14)	—	100:0

+



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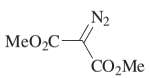
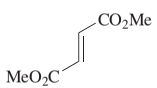


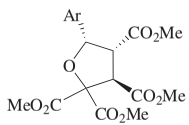
I

II



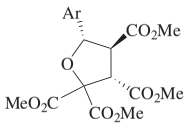
III

Catalyst, 125°



IV

+



V

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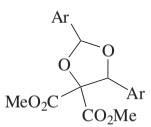
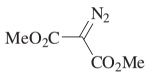
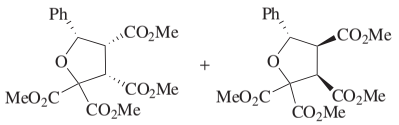
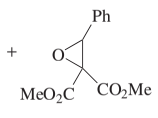
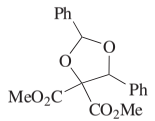
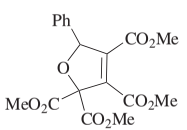
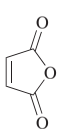
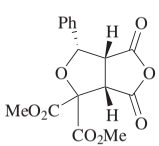
Ar	**I/II/III**	Catalyst	**IV + V**	**IV/V**	**VI**
Ph	1:6:6	—	(18)	54:46	(2)
Ph	1:2:4	Cu	(58)	54:46	(—)
4-$MeOC_6H_4$	—	Cu	(68)	54:46	(—)

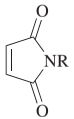
+



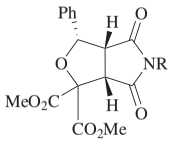
VI

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3					
			CuOTf, 80°	 **I** + **II**  **III** (—) +  **IV** (—) **I** + **II** (24), **I/II** = 55:45	241
			CuOTf, 80°	 (58)	241
			CuOTf, 80°	 (42)	241



CuOTf, 80°



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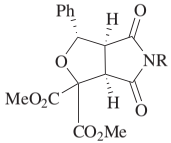

II

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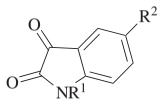
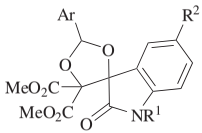
R	I + II	I/II
Me	(59)	5:1
Ph	(57)	5:1



$Rh_2(OAc)_4$, C_6H_6, 80°



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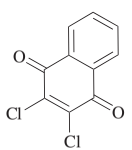
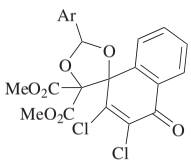
Ar	R^1	R^2	
Ph	Me	H	(76)
4-$MeOC_6H_4$	*n*-Pr	H	(93)
4-MeC_6H_4	Me	H	(81)
4-MeC_6H_4	Me	Br	(82)
4-MeC_6H_4	Et	H	(78)
4-MeC_6H_4	*n*-Pr	H	(95)
4-MeC_6H_4	Ph	H	(98)



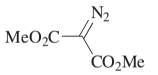
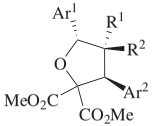
$Rh_2(OAc)_4$, C_6H_6, 80°



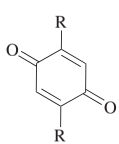
Ar	
Ph	(57)
4-$MeOC_6H_4$	(54)
4-MeC_6H_4	(77)

238

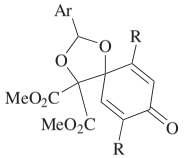
TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3					
			$Rh_2(OAc)_4$, C_6H_6, 80°		

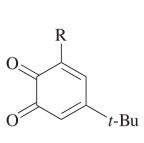
R^1	R^2	Ar^1	Ar^2		
NC	NC	Ph	Ph	(43)	240
NC	NC	4-MeC_6H_4	Ph	(49)	240
NC	NC	4-MeC_6H_4	4-FC_6H_4	(50)	240
NC	NC	4-MeC_6H_4	4-ClC_6H_4	(50)	240
NC	NC	4-MeC_6H_4	3,4-$Cl_2C_6H_3$	(44)	240
NC	NC	4-MeC_6H_4	4-MeC_6H_4	(40)	240
EtO_2C	NC	Ph	4-ClC_6H_4	(45)	240
EtO_2C	NC	4-MeC_6H_4	4-FC_6H_4	(55)	240
EtO_2C	NC	4-MeC_6H_4	4-ClC_6H_4	(55)	240
O_2N	H	Ph	Ph	(47)	239
O_2N	H	Ph	4-FC_6H_4	(50)	239
O_2N	H	Ph	4-ClC_6H_4	(47)	239
O_2N	H	Ph	3,4-$Cl_2C_6H_3$	(45)	239
O_2N	H	4-MeC_6H_4	Ph	(57)	239
O_2N	H	4-MeC_6H_4	4-FC_6H_4	(67)	239
O_2N	H	4-MeC_6H_4	4-ClC_6H_4	(76)	239
O_2N	H	4-MeC_6H_4	4-$MeOC_6H_4$	(38)	239
O_2N	H	4-MeC_6H_4	3,4-$Cl_2C_6H_3$	(58)	239
O_2N	H	4-MeC_6H_4	3-$O_2NC_6H_4$	(60)	239



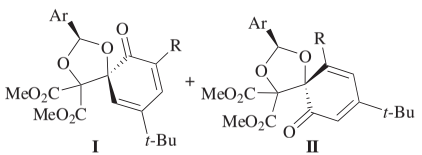
$Rh_2(OAc)_4$, C_6H_6, 80°



Ar	R		
4-$MeOC_6H_4$	Me	(51)	238
4-MeC_6H_4	H	(20)	
4-MeC_6H_4	Me	(56)	

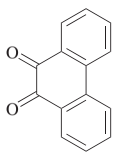


$Rh_2(OAc)_4$, C_6H_6, 80°

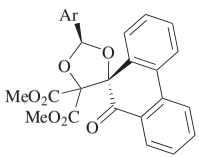


I **II**

Ar	R	**I + II**	**I/II**	
Ph	H	(45)	1:1	238
Ph	*t*-Bu	(62)	3:1	237
Ph	Ph_2CH	(65)	1.4:1	238
4-$MeOC_6H_4$	H	(33)	!:1	238
4-MeC_6H_4	H	(41)	1:1	237, 238
4-$MeOC_6H_4$	*t*-Bu	(51)	3:1	237
4-MeC_6H_4	*t*-Bu	(59)	3:1	237
3-$MeOC_6H_4$	*t*-Bu	(40)	3:1	237, 238
4-$MeOC_6H_4$	Ph_2CH	(55)	7:1	237
4-MeC_6H_4	Ph_2CH	(74)	2:1	237, 238
2,4-$(MeO)_2C_6H_3$	*t*-Bu	(34)	3:1	238

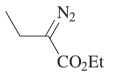
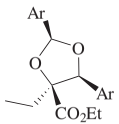
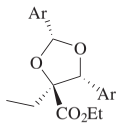
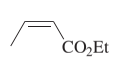
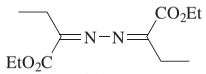


$Rh_2(OAc)_4$, C_6H_6, 80°



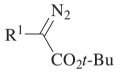
Ar		
Ph	(68)	
4-$MeOC_6H_4$	(73)	237, 238
4-MeC_6H_4	(85)	
3-$MeOC_6H_4$	(49)	
2,4-$(MeO)_2C_6H_3$	(78)	

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

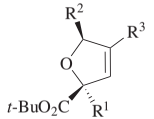
Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4					
	 *x* eq	 *x* eq	Catalyst, CH_2Cl_2	 **I** dr 90:10 +  **II** +  **III** +  **IV**	244

Ar	*x*	Catalyst	Temp (°)	I	I/II	III	IV
Ph	3	$Rh_2(OAc)_4$	−78	(26)	90:10	(18)	(2)
Ph	3	$Rh_2(Oct)_4$	−78	(42)	90:10	(5)	(1)
Ph	3	$Rh_2(tpa)_4$	−78	(33)	90:10	(9)	(2)
Ph	3	$Rh_2(Opiv)_4$	−78	(56)	90:10	(5)	(2)
Ph	4	$Rh_2(Opiv)_4$	−78	(50)	95:5	(—)	(—)
Ph	3	$Rh_2(Opiv)_4$	rt	(11)	90:10	(16)	(1)
Ph	3	$Rh_2(tfa)_3$	−78	0	—	(87)	(0)
Ph	3	$Rh_2(esp)_2$	−78	(44)	90:10	(7)	(5)
Ph	3	**10b**	−78	(23) (*rac*)	90:10	(17)	(1)
Ph	3	(*R*)-**6**	−78	(0)	—	(7)	(44)
4-FC_6H_4	4	$Rh_2(Opiv)_4$	−78	(66)	>95:5	(—)	(—)
3-ClC_6H_4	4	$Rh_2(Opiv)_4$	−78	(71)	>95:5	(—)	(—)
4-$O_2NC_6H_4$	4	$Rh_2(Opiv)_4$	−78	(59)	90:10	(—)	(—)
2-ethynylphenyl	4	$Rh_2(Opiv)_4$	−78	(54)	>95:5	(—)	(—)
2-naphthyl	4	$Rh_2(Opiv)_4$	−78	(64)	90:10	(—)	(—)

C_{4-6}



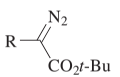
$Rh_2(Opiv)_4$, CH_2Cl_2, −78°



106

R^1	R^2	R^3		dr
Et	*n*-Bu—≡	MeO_2C	(86)	>95:5
Et	Ph	MeO_2CCH_2	(76)	88:12
Et	2-MeC_6H_4	$MeOCCH_2$	(77)	92:8
n-Bu	4-FC_6H_4	MeO_2C	(83)	>95:5
n-Bu	Ph—≡	MeO_2C	(90)	>95:5

C_{4-9}

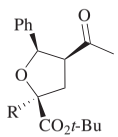


x eq

y eq

z eq

$Rh_2(Opiv)_4$, CH_2Cl_2, −78°



R	*x*	*y*	*z*		dr
Et	1.3	1.0	1.1	(56)	>95:5
Et	1.5	1.0	1.1	(69)	>95:5
Et	1.7	1.0	1.1	(77–80)	>95:5
Et	1.9	1.0	1.1	(76)	>95:5
Bn	1.0	1.1	4.0	(53)	—
Bn	1.5	1.0	4.0	(78)	—
Bn	2.0	1.0	4.0	(78)	—
Bn	1.5	1.0	2.0	(85)	—
Bn	1.5	1.0	1.1	(81)	—
Bn	1.3	1.0	1.1	(84)	—
Bn	1.1	1.0	1.1	(76)	—
Bn	1.5	1.0	1.1	(16)[f]	—

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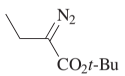
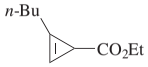
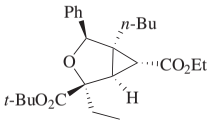
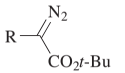
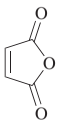
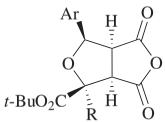
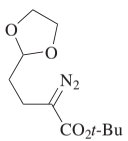
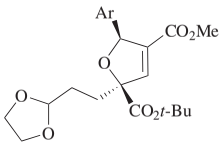
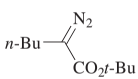
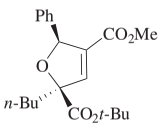
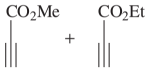
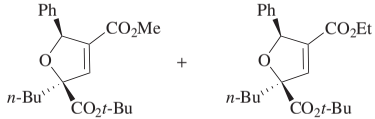
TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4					
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°	 (62) dr >95:5	106
C_{4-9} 			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°		106
				R Ar dr Et 3-ClC_6H_4 (68) 91:9 Bn Ph (73) 95:5	
C_5					
	 Ar = 2-MeC_6H_4		$Rh_2(Opiv)_4$, CH_2Cl_2, −78°	 (97) dr >95:5	106
C_6					
			1. $Rh_2(Opiv)_4$, CH_2Cl_2, −78° 2. Dipolarophile, −78° to rt	 (—)	106



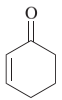
1:1

$Rh_2(Opiv)_4$, CH_2Cl_2, −78°

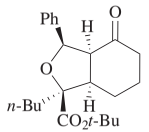


I + **II** (—), **I**/**II** = 1:1

106



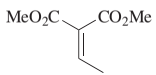
$Rh_2(Opiv)_4$, CH_2Cl_2, −78°



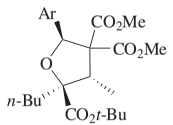
(77) dr >95:5

106

Ar = 4-ClC_6H_4



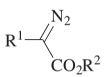
$Rh_2(Opiv)_4$, CH_2Cl_2, −78°



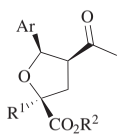
(75) dr >95:5

106

C_{7-9}



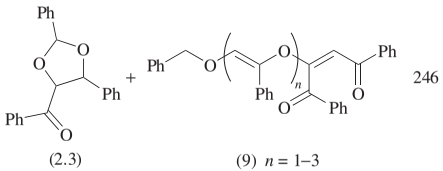
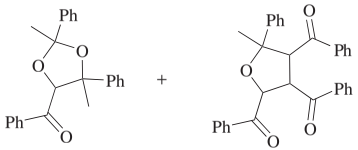
$Rh_2(Opiv)_4$, CH_2Cl_2, −78°



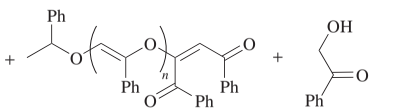
106

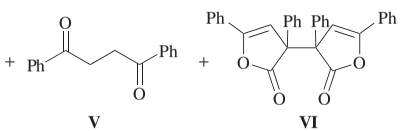
R^1	R^2	Ar		dr
s-C_5H_{11}	*t*-Bu	4-ClC_6H_4	(73)	>95:5
n-C_6H_{13}	*t*-Bu	Ph	(51)	>95:5
Bn	Et	4-$MeOC_6H_4$	(80)	>95:5
Bn	*t*-Bu	Ph	(73)	>95:5
Bn	*i*-Bu	$Me_2(OH)C{-}{\equiv}{-}C_6H_4$	(59)	94:6

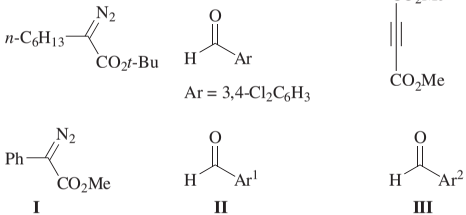
TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

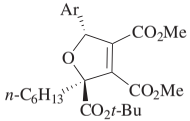
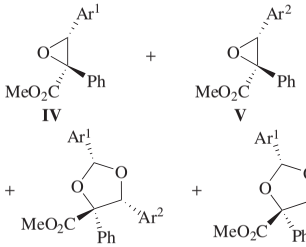
Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8					
			$Cu(acac)_2$, C_6H_6, 80°, method B[d]	 (2.3) + (9) n = 1–3 + copolymers	246
		$Cu(acac)_2$, C_6H_6, 80°	 **I** + **II**	246

Method[d]	I	II	III	IV	V	VI
A	(—)	(29)	(44)	(1)	(—)	(—)
B	(7)	(8.3)	(10)	(1.7)	(1)	(1)


III n = 1–3 **IV**

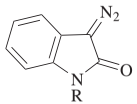
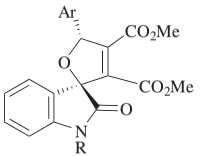

V **VI**



$Rh_2(Opiv)_4$, CH_2Cl_2, −78°		(63) dr >95:5	106
$Rh_2(OAc)_4$, CH_2Cl_2, reflux			236

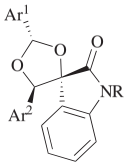
Ar^1	Ar^2	I/II/III	IV[e]	V[e]	VI + VII[f]	VI/VII
Ph	$2,4\text{-}(O_2N)_2C_6H_3$	1.5:2:1	(—)	(—)	(85)	85:15
$2\text{-}MeOC_6H_4$	$2,4\text{-}(O_2N)_2C_6H_3$	1.5:2:1	(—)	(—)	(90)	83:17
$4\text{-}MeOC_6H_4$	$4\text{-}O_2NC_6H_4$	1:2:2	(13)	(11)	(50)	45:55
$4\text{-}MeOC_6H_4$	$2,4\text{-}(O_2N)_2C_6H_3$	1.5:2:1	(—)	(—)	(95)	81:19
piperonyl	$2,4\text{-}(O_2N)_2C_6H_3$	1.5:2:1	(—)	(—)	(94)	81:19
$2,4\text{-}(MeO)_2C_6H_3$	$4\text{-}O_2NC_6H_4$	1.5:2:1	(—)	(—)	(78)	43:57
$2,4\text{-}(MeO)_2C_6H_3$	$4\text{-}O_2NC_6H_4$	1:2:2	(—)	(—)	(61)	43:57
$2,4,6\text{-}(MeO)_3C_6H_2$	$2\text{-}O_2NC_6H_4$	1:2:2	(—)	(—)	(65)	60:40
$2,4,6\text{-}(MeO)_3C_6H_2$	$4\text{-}O_2NC_6H_4$	1:2:2	(—)	(—)	(74)	45:55
$2,4,6\text{-}(MeO)_3C_6H_2$	$2,4\text{-}(O_2N)_2C_6H_3$	1:2:2	(—)	(—)	(80)	77:23
$2,4,6\text{-}(MeO)_3C_6H_2$	$4\text{-}NCC_6H_4$	1:2:2	(—)	(—)	(71)	40:60
$2,4,6\text{-}(MeO)_3C_6H_2$	$4\text{-}CF_3C_6H_4$	1:2:2	(—)	(—)	(63)	32:68
$2,4,6\text{-}(MeO)_3C_6H_2$	$2\text{-}(CHO)C_6H_4$	1:2:2	(—)	(—)	(50)	43:57
$3\text{-}MeC_6H_4$	$2,4\text{-}(O_2N)_2C_6H_3$	1.5:2:1	(—)	(—)	(91)	84:16

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 			$Rh_2(OAc)_4$, CH_2Cl_2, rt		88

R	Ar	
H	Ph	(25)
Me	Ph	(62)
Me	4-$MeOC_6H_4$	(83)
Me	3-MeO-4-HOC_6H_3	(70)
CH_2=$CHCH_2$	Ph	(55)
CH_2=$CHCH_2$	4-$MeOC_6H_4$	(94)
CH_2=$CHCH_2$	3-MeO-4-HOC_6H_3	(79)
CH≡CCH_2	Ph	(58)
CH≡CCH_2	4-$MeOC_6H_4$	(91)
Bn	Ph	(64)
Bn	4-$MeOC_6H_4$	(96)
Bn	3-MeO-4-HOC_6H_3	(77)
$MeC_6H_4CH_2$	Ph	(50)
$MeC_6H_4CH_2$	4-$MeOC_6H_4$	(87)
Me	2-furyl	(68)
CH_2=$CHCH_2$	2-furyl	(80)
CH≡CCH_2	2-furyl	(57)
Bn	2-furyl	(81)
Me	9-anthryl	(67)
CH_2=$CHCH_2$	9-anthryl	(56)
CH_2=$CHCH_2$	1-pyrenyl	(85)

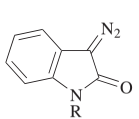
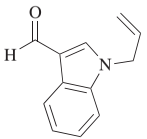
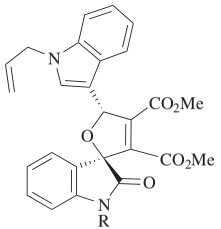
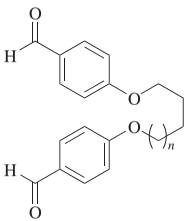
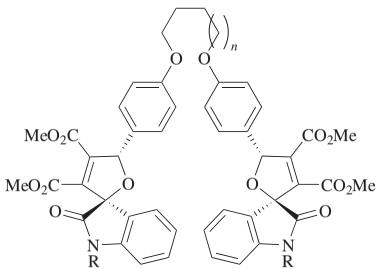
$Rh_2(OAc)_4$, CH_2Cl_2, rt



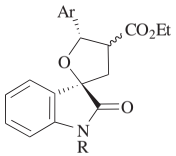
344

R	Ar^1	Ar^2	
Me	4-$MeOC_6H_4$	2-$O_2NC_6H_4$	(82)
Me	4-$MeOC_6H_4$	4-$O_2NC_6H_4$	(80)
Me	4-$MeOC_6H_4$	3-$O_2NC_6H_4$	(78)
Me	3,4-$(MeO)_2C_6H_3$	2-$O_2NC_6H_4$	(80)
Me	3,4-$(MeO)_2C_6H_3$	4-$O_2NC_6H_4$	(75)
Me	naphthyl	4-$O_2NC_6H_4$	(80)
Me	naphthyl	3-$O_2NC_6H_4$	(70)
Me	4-$MeOC_6H_4$	2-ClC_6H_4	(55)
Me	4-$MeOC_6H_4$	3-FC_6H_4	(60)
Me	4-$MeOC_6H_4$	3-BrC_6H_4	(60)
Bn	4-$MeOC_6H_4$	4-$O_2NC_6H_4$	(85)
Bn	4-$MeOC_6H_4$	2-$O_2NC_6H_4$	(85)
Bn	Ph	2-$O_2NC_6H_4$	(70)

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8					
			$Rh_2(OAc)_4$, CH_2Cl_2, rt	 R: Me (68); CH_2=$CHCH_2$ (75)	88
			$Rh_2(OAc)_4$, CH_2Cl_2, rt	 *n*, R: 0, CH_2=$CHCH_2$ (83); 1, CH_2=$CHCH_2$ (75); 0, Bn (72); 1, $MeC_6H_4CH_2$ (76)	88

$Rh_2(OAc)_4$, CH_2Cl_2, rt



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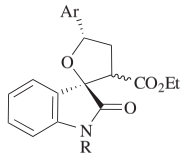
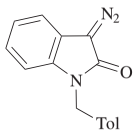


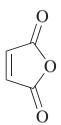
88

I **II**

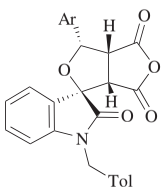
R	Ar	I + II	I/II
$CH{\equiv}CCH_2$	4-$MeOC_6H_4$	(67)	59:41
$MeC_6H_4CH_2$	2-furyl	(33)	51:49



Ar = 4-$MeOC_6H_4$



$Rh_2(OAc)_4$, CH_2Cl_2, rt



(37)

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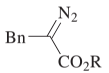
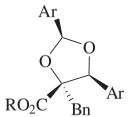
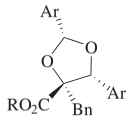
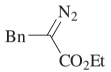
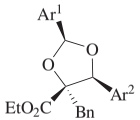
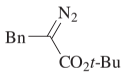
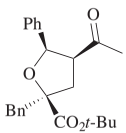
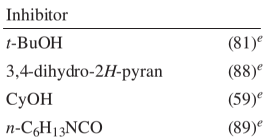
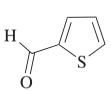
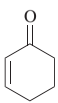
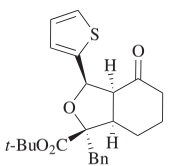
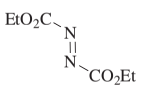
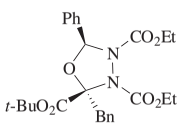
TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

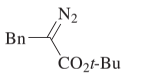
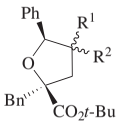
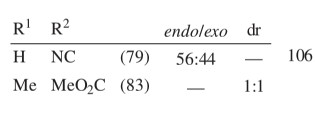
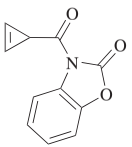
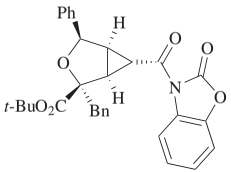
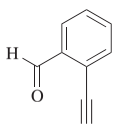
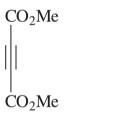
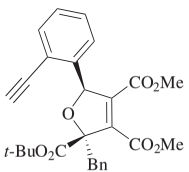
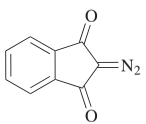
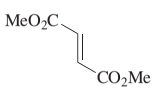
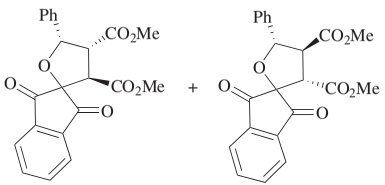
Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9					
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°	 **I** +  **II**	244

R	Ar	I + II	dr
Et	2-thienyl	(59)	85:15
Et	Ph	(60)	>92:8
Et	4-FC_6H_4	(65)	90:10
Et	2-ClC_6H_4	(58)	>95:5
Et	3-ClC_6H_4	(54)	>95:5
Et	4-ClC_6H_4	(57)	>95:5
Et	4-$O_2NC_6H_4$	(56)	86:14
Et	4-$MeOC_6H_4$	(58)	80:20
Et	2-MeC_6H_4	(58)	84:14:2
Et	2-naphthyl	(66)	87:13
t-Bu	2-thienyl	(64)	>95:5
t-Bu	4-$O_2NC_6H_4$	(72)	94:6
t-Bu	4-$MeOC_6H_4$	(67)	83:9:8
t-Bu	2-MeC_6H_4	(60)	94:6
t-Bu	2-naphthyl	(78)	>95:5

	 $Ar^1 = 4\text{-}ClC_6H_4$	 $Ar^2 = 4\text{-}FC_6H_4$	1. $Rh_2(Opiv)_4$, CH_2Cl_2, −78°, carbonyl substrate 2. Dipolarophile, −78° to rt		(—)	244
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°			106
		$Rh_2(Opiv)_4$, CH_2Cl_2, −78°		(63) dr >95:5	106
		$Rh_2(Opiv)_4$, CH_2Cl_2, −78°		(57) dr >95:5	106

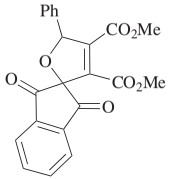
Inhibitor	
t-BuOH	(81)[e]
3,4-dihydro-2*H*-pyran	(88)[e]
CyOH	(59)[e]
$n\text{-}C_6H_{13}NCO$	(89)[e]
(*R*)-4-benzyloxazolidin-2-one	(75)[e]
$4\text{-}ClC_6H_4OH$	(88)[e]
$4\text{-Me-2,6-}Br_2C_6H_2OH$	(87)[e]
$2\text{-}BrC_6H_4CH_2CN$	(78)[e]
PhCH=NPh	(46)[e]
$Ph_2NCH_2CO_2Et$	(60)[e]
indole	(74)

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9					
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°	 	106
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°	 (63) dr >95:5	106
			$Rh_2(Opiv)_4$, CH_2Cl_2, −78°	 (99) dr >95:5	106
			$Rh_2(OAc)_4$, 4 Å MS, DCE, 80°	 **I** + **II** (61), **I**/**II** 59:41	340

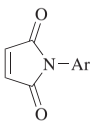
R^1	R^2		*endo*/*exo*	dr
H	NC	(79)	56:44	—
Me	MeO_2C	(83)	—	1:1

$Rh_2(OAc)_4$, 4 Å MS, DCE, 80°

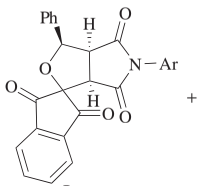


(55)

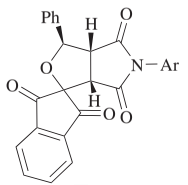
340



$Rh_2(OAc)_4$ (x mol %)



+



340

diazo/aldehyde/dipolarophile = 1:4:4

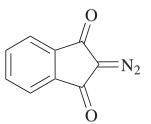
Ar = 3,4-$Cl_2C_6H_3$

I **II**

x	Additive	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**
2	—	DCE	80	1	(35)	79:21
2	—	DCE	80	1	(60)	71:29
1	—	DCE	80	2	(61)	72:28
1	4 Å MS	DCE	80	2	(43)	79:21
1	4 Å MS	DCE	80	2	(78)	72:28
—	—	toluene	reflux	—	(<5)[g]	—

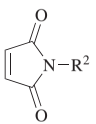
TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9					



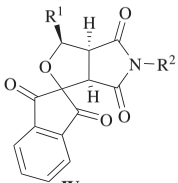
I

II



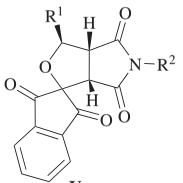
III

$Rh_2(OAc)_4$



IV

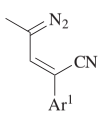
+



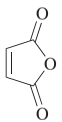
V

R^1	R^2	I/II/III	Additive	Solvent	Temp (°)	IV + V	IV/V	
Ph	Et	1:1:4	4 Å MS	DCE	80	(47)	75:25	340
Ph	Ph	1:1:4	4 Å MS	DCE	80	(65)	67:33	340
Ph	3-ClC_6H_4	1:1:4	4 Å MS	DCE	80	(58)	69:31	340
Ph	4-$O_2NC_6H_4$	1:1:4	4 Å MS	DCE	80	(40)	70:30	340
Ph	4-$MeOC_6H_4$	1:1:4	4 Å MS	DCE	80	(51)	66:34	340
4-$O_2NC_6H_4$	3,4-$Cl_2C_6H_3$	1:1:4	4 Å MS	DCE	80	(60)	65:35	340
4-$MeOC_6H_4$	3,4-$Cl_2C_6H_3$	1:1:4	4 Å MS	DCE	80	(61)	80:20	340
3,4-OCH_2O-C_6H_3	3,4-$Cl_2C_6H_3$	1:1:4	4 Å MS	DCE	80	(63)	74:26	340
3,4-OCH_2O-C_6H_3	3,4-OCH_2O-C_6H_3	1:1:4	4 Å MS	DCE	80	(60)	67:33	340
3,4-OCH_2O-C_6H_3	3,4-OCH_2O-C_6H_3	—	—	C_6H_6	reflux	(8)	—	341
(*E*)-C_6H_5CH=CH	3,4-$Cl_2C_6H_3$	1:1:4	4 Å MS	DCE	80	(43)	72:28	340
(*E*)-C_6H_5CH=CH	4-AcC_6H_4	1:1:4	4 Å MS	DCE	80	(53)	74:26	340

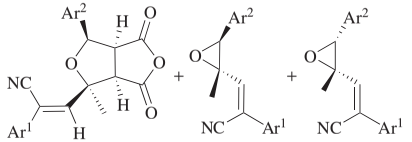
C_{11}



$Ar^1 = 4\text{-}ClC_6H_4$



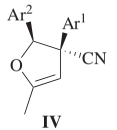
$Rh_2(OAc)_4$



I **II** **III**

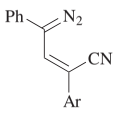
342

Ar^2	Solvent	Temp (°)	**I**	**I/II/III/IV**
$4\text{-}ClC_6H_4$	DCE	0	(68)	—
$4\text{-}ClC_6H_4$	C_6H_6	50	—	88:0:12:0
$4\text{-}O_2NC_6H_4$	C_6H_6	50	—	77:0:23:0

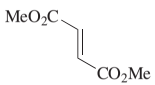


IV

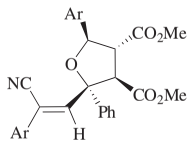
C_{16}



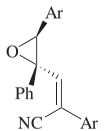
$Ar = 4\text{-}ClC_6H_4$



$Rh_2(OAc)_4$, DCE, 0°

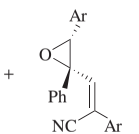


I (39)

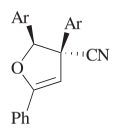


II (—)

342



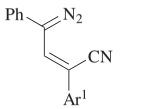
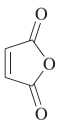
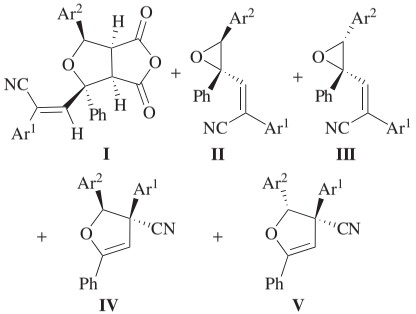
III (—)



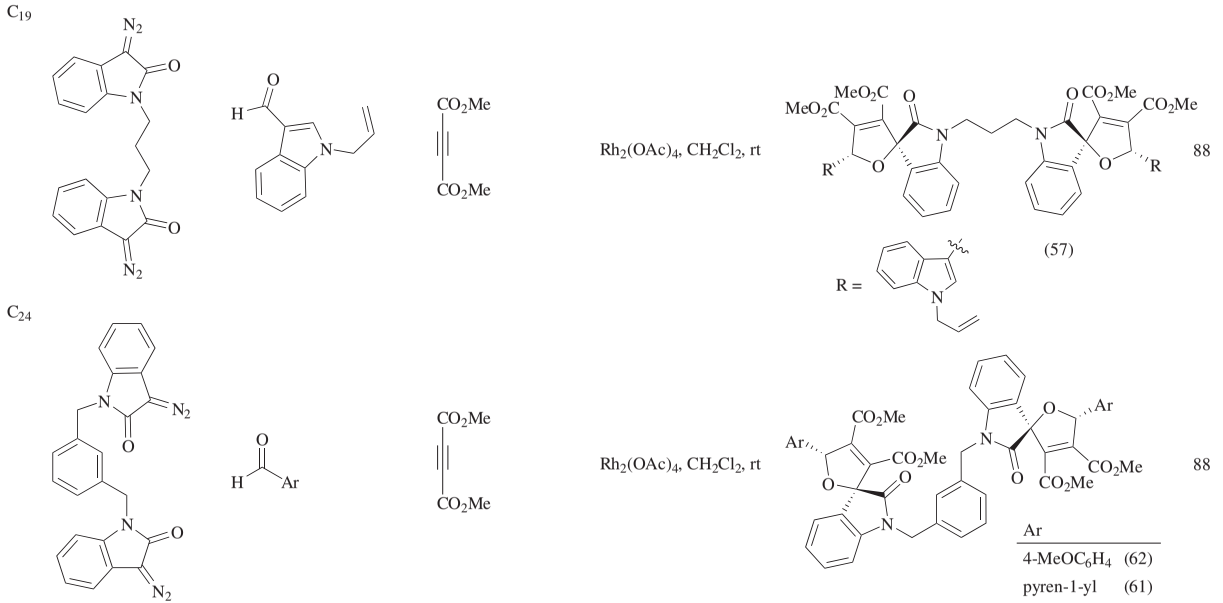
IV (—)

I/II/III/IV = 48:17:24:11

TABLE 20. CYCLOADDITIONS OF ACYCLIC CARBONYL YLIDES FROM ALDEHYDES, KETONES, OR IMIDES (*Continued*)

Diazo Substrate	Carbonyl Substrate	Dipolarophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}					
 $Ar^1 = 4\text{-}ClC_6H_4$			$Rh_2(OAc)_4$	 **I** **II** **III** **IV** **V**	

Ar^2	Solvent	Temp (°)	**I** + **II** + **III** + **IV** + **V**	**I/II/III/IV/V**	
$4\text{-}ClC_6H_4$	C_6H_6	50	(71	76:8:8:8:0	342, 343
$4\text{-}ClC_6H_4$	DCE	0	(100)	**I** only	342
$4\text{-}ClC_6H_4$	DCE	40	(—)	84:4:5:6:0	342
$4\text{-}ClC_6H_4$	DCE	50	(—)	76:8:8:8:0	342
$4\text{-}ClC_6H_4$	DCE	60	(—)	68:10:10:12:0	342
$4\text{-}ClC_6H_4$	DCE	80	(—)	56:10:17:17:0	342
$4\text{-}O_2NC_6H_4$	C_6H_6	50	(—)	16:11:18:51:4	342
$4\text{-}MeOC_6H_4$	C_6H_6	50	(—)	76:0:2:22:0	342



[a] The addition time of the diazo compound was 10 hours.

[b] The reaction was carried out at −10°.

[c] The reaction was carried out at room temperature.

[d] Method A: a solution of the diazo compound was added dropwise to a solution of the carbonyl compound and $Cu(acac)_2$ in C_6H_6 at 80° over 2 hours; method B: a mixture of diazo compound, $Cu(acac)_2$, and the carbonyl compound was gradually warmed under N_2.

[e] Yields are based on the ^1H NMR spectra of the crude products.

[f] The numbers are the yields of isolated products.

[g] The major products are derived from the insertion of the carbene into the solvent, toluene.

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