

Intermolecular Metal-Catalyzed Carbenoid Cyclopropanations

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1. Introduction

The metal-catalyzed decomposition of diazo compounds in the presence of alkenes is a well-established reaction. Since the original *Organic Reactions* review on the reaction of ethyl diazoacetate with alkenes and aromatic compounds in 1970, (1) several new developments have revolutionized this area of chemistry. Most notably, major advances have been made in catalyst design such that highly chemoselective, diastereoselective and enantioselective carbenoid transformations can now be achieved. Furthermore, it has been recognized that a wide array of carbenoid structures can be utilized in this chemistry, leading to a broad range of synthetic applications.

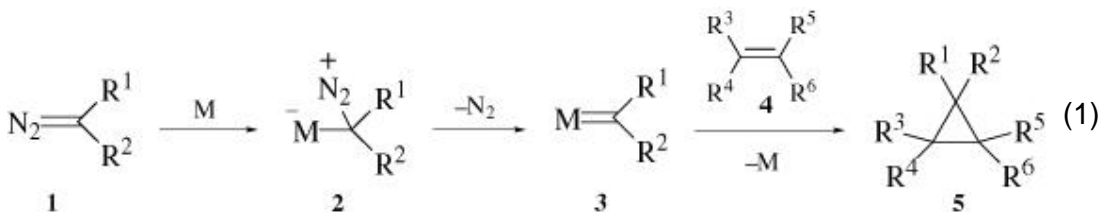
This chapter comprises coverage of the metal-catalyzed intermolecular cyclopropanations of diazo compounds containing at least one adjacent electron-withdrawing group. The coverage of diazoacetate chemistry will be limited to material since 1970 because the previous *Organic Reactions* review (1) covers the earlier literature. The alkene component is limited to alkenes, dienes, furans, and pyrroles because these are the systems that have resulted in the greatest developments since the 1970 review. Metal-carbenoid intermediates derived from diazo compounds undergo a variety of useful reactions, including cyclopropanation, insertion, and ylide formation. In recent years several excellent reviews have appeared on various aspects of this chemistry. (2-28) Three recent reviews have focused on asymmetric intermolecular cyclopropanations. (3, 29, 30) Several books and reviews on carbenoid chemistry have major sections on intermolecular cyclopropanations. Because of the historical central prominence of carbenoids derived from diazoacetates, most reviews have tended to focus on this class of carbenoids. In this chapter, a comparison is presented of the chemical differences that exist among the major classes of carbenoids that contain adjacent electron-withdrawing groups. The extensive nature of the topic precludes coverage of related reactions such as the metal-catalyzed decomposition of diazoalkanes, (31) phenyldiazoalkanes, (32) or vinyldiazoalkanes (33) that lack adjacent electron-withdrawing functionality. Other cyclopropanation reactions such as the Simmons-Smith reaction, (34-36) photochemical or thermal decomposition of diazo compounds in the presence of alkenes, (1) and cyclopropanation using stoichiometric metal carbenes (37, 38) are not

covered.

2. Mechanism

Despite the great synthetic utility of diazo compounds in cyclopropanations, definitive mechanistic studies on the metal-catalyzed cyclopropanations are lacking. (39-42) Reasonable mechanistic models have been rationalized on the basis of product distribution, and especially the stereochemical outcome of various carbenoid reactions. (8, 9, 13) Because of the rapid catalytic turnovers of these reactions, structural information about the intermediates is difficult to obtain. Recently, some significant advances have been made that will likely have a major impact on the mechanistic understanding of these transformations. Stable rutheniumcarbenoid complexes have been characterized by X-ray crystallography. (43-45) As these systems are also capable of inducing catalytic carbenoid transformations, the X-ray crystallographic data lead to definitive information about the key metal carbenoid intermediate in catalytic reactions. Additionally, some major advances have been made in the use of molecular modeling to probe the structure of carbenoid intermediates, (46-48) and as more advanced computational methods are used, very useful information regarding the validity of various carbenoid transition state models should be forthcoming.

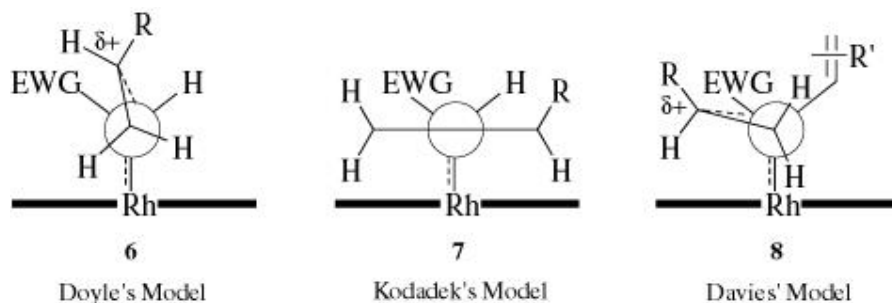
It is generally agreed that the reaction proceeds as shown in Eq. 1. (49) Interaction of diazo compound **1** with the metal forms diazonium complex **2**, which then extrudes nitrogen to form carbenoid intermediate **3**.



Reaction of alkene **4** with **3** forms cyclopropane **5** and regenerates the active catalyst. For most catalysts, attack of the alkene on the carbenoid is generally considered to occur without coordination of the alkene to metal, although there is evidence that prior coordination does occur for palladium-based catalysts and copper(I) triflate. (37, 50) An alternative view that the reaction involves metallocyclobutane intermediates analogous to the chemistry of Fischer carbenes has been presented in a few publications, (51-54) although supporting evidence is limited.

If the cyclopropanation does occur without prior coordination of the alkene, the trajectory of the approach of the alkene to the metal-carbene complex becomes a critical element for control of regiochemistry and stereochemistry.

The most established model for alkene approach to the metal-carbenoid complex was proposed by Doyle to explain the stereochemistry in cyclopropanations by diazoacetates.



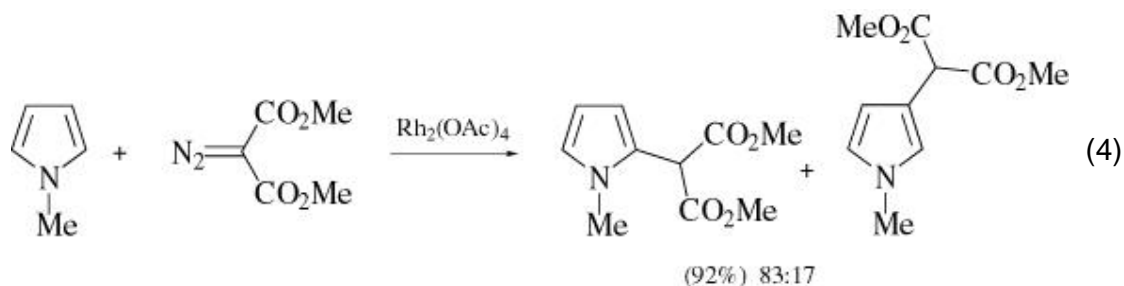
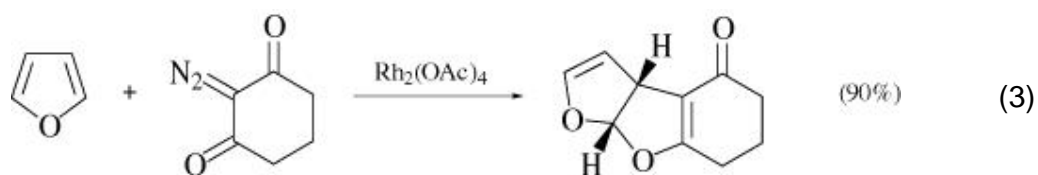
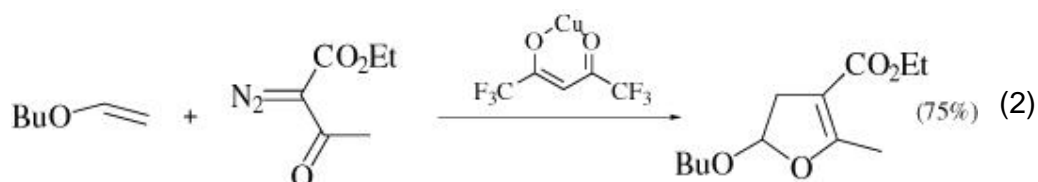
In the latest version of the Doyle model (**6**), (**8**, **9**, **32**, **49**) the alkene is considered to approach the carbene close to end-on, and cyclopropanation occurs in a nonsynchronous mode with charge build-up in the transition state. Interaction between the ester of the carbenoid and the partial positive charge of the alkene in the transition state is a major cause of the stereocontrol. The metal surface is considered to be a “wall” and the stereochemistry is controlled by ensuring that the bulky functionality of the alkene points away from the metal surface. A similar model was used to explain the diastereoselectivity observed in cyclopropanations with nitrodiazomethane. (**55**)

A second model, **7**, was developed by Kodadek to explain unusual *Z*-stereoselectivity of bulky rhodium porphyrin catalysts. (**56**, **57**) The alkene is considered to approach the carbene in a side-on approach with no charge build-up in the transition state. Evidence to support the lack of charge build-up was seen in the lack of alkene substituent effects on the relative rates of cyclopropanations, and the absence of deuterium isotope effects. To complete the cyclopropanation, rotation of the alkene, either inward or outward, is required. The direction of this rotation is dependent on the steric effects of the catalyst and the carbenoid substituents.

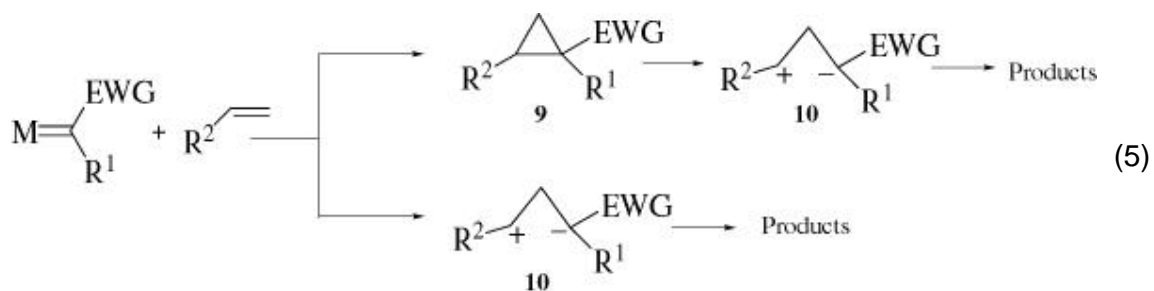
A third model has been proposed by Davies to explain the extremely high diastereoselectivity that occurs in cyclopropanation reactions of vinyl diazoacetates and aryl diazoacetates. (**6**, **58**) This model, **8**, is a hybrid of models **6** and **7**. The alkene approaches the vinylcarbenoid close to side-on in a nonsynchronous mode. The approach occurs on the side of the electron-withdrawing group with the bulky functionality of the alkene pointing away from the face of the rhodium complex. A *trans* alkene is unreactive because it is unable to avoid having a substituent pointing directly toward the rhodium surface. As the reaction proceeds, the alkene would need to rotate outward to form the cyclopropane ring, where R would end up on the same side as the vinyl group, leading to the observed stereochemistry. The fact that the diastereocontrol is enhanced by electron-donating groups on the alkene

(59) while trans alkenes are unreactive (58) is good evidence to support this side-on nonsynchronous model. The subtle differences between these models may reflect that the actual interaction between the carbenoid and alkene is variable, and is dependent upon the types of carbenoid and catalyst employed.

In certain instances the product isolated in the metal-catalyzed reaction of diazo compounds with unsaturated systems is not the simple cyclopropanated product. These types of reactions are especially prevalent when the carbenoid contains two electron-withdrawing groups and the alkene or aromatic system has electron-donating substituents. (60-64) Examples of these types of reactions are shown in Eqs. 2, 3, 4. (65-68)



When the cyclopropane is not the isolated product there is often ambiguity about whether these products are derived directly from the carbenoid on reaction with the alkene component or from rearrangement of the initially formed cyclopropane **9** (Eq. 5). (49) The zwitterionic intermediate **10** could in principle be formed from either source.



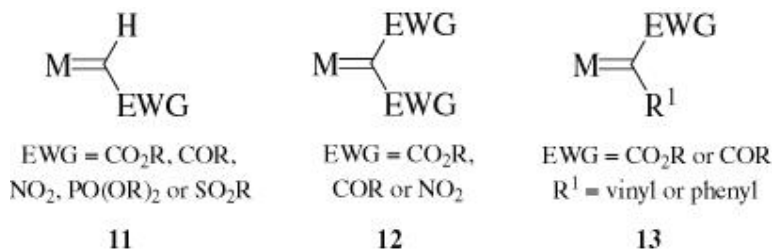
Furthermore, depending on the reaction, the zwitterionic intermediate may still be associated with the catalyst, which would enable the catalyst to affect asymmetric induction and product distribution. As cyclopropanation and formation of products derived from zwitterionic intermediates are often competing processes, (60-64) both reactions are covered in this review.

In recent years, with the advent of numerous excellent methods for asymmetric induction in various carbenoid transformations, several transition state models have been developed to explain how asymmetric induction is obtained. (6, 14, 49, 69, 70) A discussion of the various predictive models that have been proposed for asymmetric induction will not be presented in this chapter. Many of these models require further verification before it would be appropriate to discuss them in a review of this type.

3. Scope and Limitations

3.1. Cyclopropanation of Alkenes

The most widely exploited reaction of carbenoids is the cyclopropanation of alkenes. In this discussion, the carbenoids will be divided into three major groups (11-13), because the chemistry is very much dependent upon the carbenoid structure.



The first group will be carbenoids containing a single electron-withdrawing group. This will include carbenoids derived from diazoacetates and related systems. (8, 9, 15, 20, 71) The diazoacetate system is by far the most extensively studied system. In recent years, the development of chiral catalysts to achieve asymmetric cyclopropanations with the diazoacetate system has been an immensely popular field of research. (3, 6, 14, 30, 49, 69) The second group will be carbenoids containing two electron-withdrawing groups. This includes carbenoids derived from diazoacetoacetates, diazomalonates, (61) and diazodiketones. Also, carbenoids derived from diazopyruvates (72) are included with this group. Often, the products from this group of carbenoid precursors are not cyclopropanes but isomeric structures derived from zwitterionic intermediates. (60-62) The third group will be carbenoids containing both an electron-withdrawing group and an electron-donating group such as vinyl or phenyl. (4-7) This includes carbenoids derived from vinyl diazoacetates, phenyl diazoacetates, and related systems. Carbenoids containing a combination of donor and acceptor groups exhibit unique stereoselectivity in their chemistry (59, 73, 74) that warrants their consideration as a separate class.

3.2. Carbenoids Derived from Diazoacetates and Related Systems

The decomposition of alkyl diazoacetates in the presence of alkenes is an excellent method for the synthesis of cyclopropanes (Eq. 6). (1, 8, 9, 15, 20, 49, 71) The reaction is extremely general, with electron-rich, electron-neutral, and even slightly electron-deficient alkenes subject to cyclopropanation.

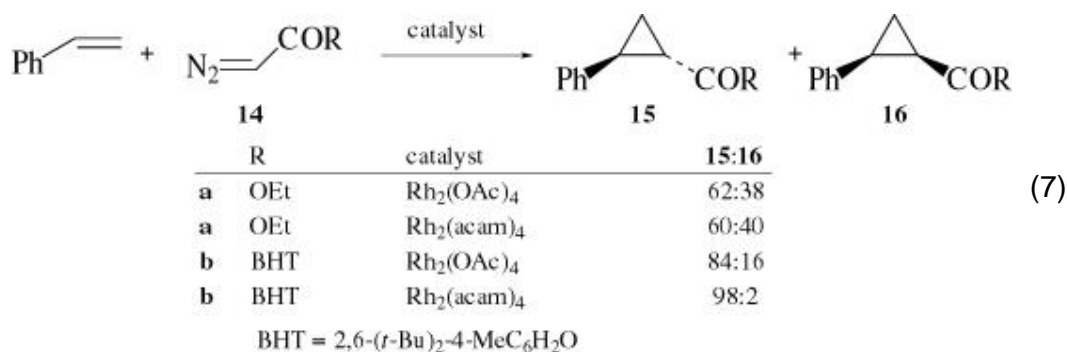


Even though monosubstituted alkenes are the most common substrates, a range of substitution patterns, from monosubstituted to tetrasubstituted, can be tolerated. The traditional catalysts for these transformations were copper based, (1) but in recent years dirhodium complexes have become the catalysts of choice for most reactions. (75) Not only do these catalysts permit very mild reaction conditions, but also fine-tuning of the reaction is possible by appropriate choice of dirhodium ligands. The most commonly used catalyst is dirhodium tetraacetate. (76, 77) Highly electron-deficient ligands such as trifluoroacetate lead to more electrophilic carbenoids while electron-donating ligands such as acetamide lead to less reactive and more selective carbenoids. (78) Complexes of a number of other metals, such as palladium, (79, 80) ruthenium, (51, 81-84) cobalt, (85-89) osmium, (90, 91) and iron (92) have also been used as catalysts in these diazo decomposition reactions. One of the most common side-reactions in the chemistry of this class of carbenoids is the formation of carbene dimers, (1, 12, 93) although in general this problem can be alleviated by using very slow addition of the diazo compound to the reaction mixture. (94)

Similar cyclopropanations have been carried out with a range of other diazo compounds containing a single electron-withdrawing group. These include keto, (95) nitro, (96) sulfonyl, (97) and phosphonyl (98) groups. In many instances the reported yields are relatively low, but several of the studies were carried out using copper catalysis, and it would be reasonable to expect that greatly improved yields would be achieved in many instances if the dirhodium tetracarboxylates were used as catalysts.

3.2.1. Diastereoselectivity

One of the major limitations of cyclopropanations by diazoacetates is that, in general, the cyclopropanations are not particularly stereoselective. (49, 71) Standard reactions of styrene with ethyl diazoacetates **14a** and **14b** yield the diastereomeric products **15** and **16** (Eq. 7), their *E* to *Z* ratios dependent upon the size of the ester moiety. The use of ethyl diazoacetate (**14a**) results in a diastereoselectivity of less than 2:1 favoring the *E* isomer (**15a**) over the *Z* isomer (**16a**). Considerable enhancement in the diastereoselectivity can be achieved by using bulky ester derivatives, such as that derived from 3,5-*bis*(*tert*-butyl)-4-hydroxytoluene (**14b**). (78) In combination with rhodium acetamide $\text{Rh}_2(\text{acam})_4$ as catalyst, the diastereoselectivity of the reaction of styrene with **14b** is improved to 98:2 *E*:*Z* (**15b**:**16b**). The diastereoselectivity of diazoacetate cyclopropanations is only moderately influenced by most catalysts. (8, 9, 15)

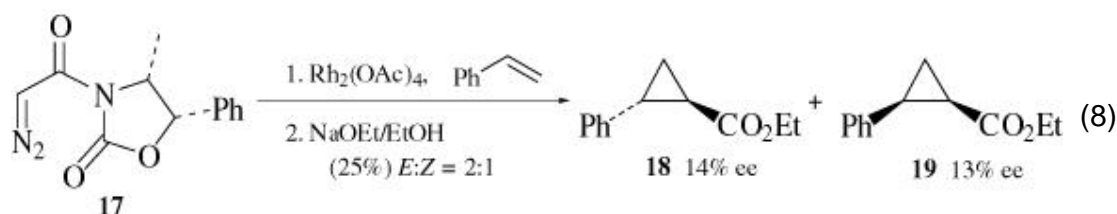


(7)

If the catalysts are extremely bulky, however, such as dirhodium tetra(2,6-disubstituted benzoates) (99) or sterically crowded rhodium porphyrins, (100-102) the diastereoselectivity can be altered leading to a slight preference for the *Z* isomer. A major improvement in diastereoselectivity favoring the formation of *E* cyclopropanes has been discovered recently for reactions catalyzed by ruthenium complexes. (103-107)

3.2.2. Asymmetric Induction Using Chiral Auxiliaries

Several attempts have been made to develop an asymmetric cyclopropanation using chiral auxiliaries although these have not been very successful. (106, 108-111) Cyclopropanation with *t*-menthyl diazoacetate results in high yields but the asymmetric induction is very poor, yielding <2% enantiomeric excess (ee). (112) Attempts to enhance the asymmetric induction by using auxiliaries containing a carbonyl group that may interact with the carbenoid have also been carried out. (110) This approach has not been effective with the diazoacetate system. Reaction of 17 with styrene results in the formation of cyclopropanes 18 and 19 with low enantioselectivity (Eq. 8). (110)

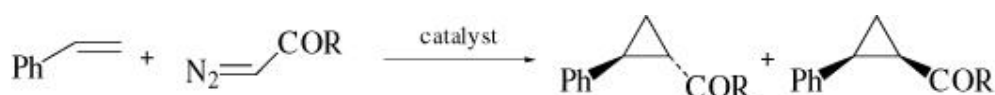
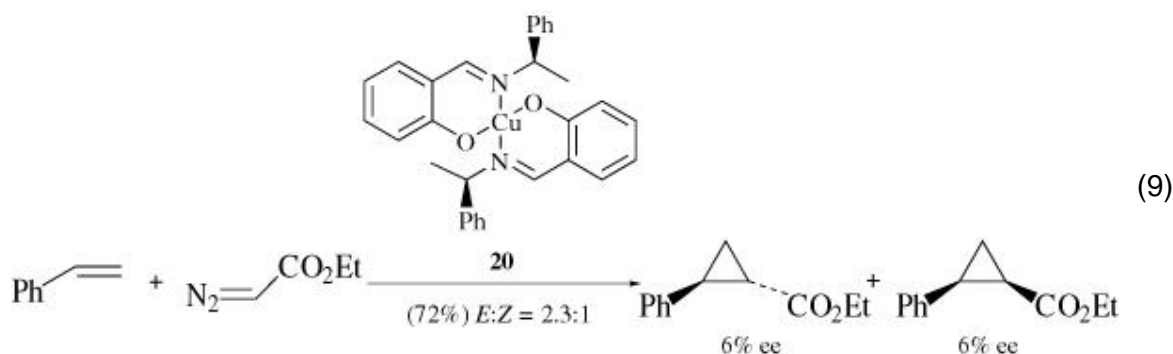


(8)

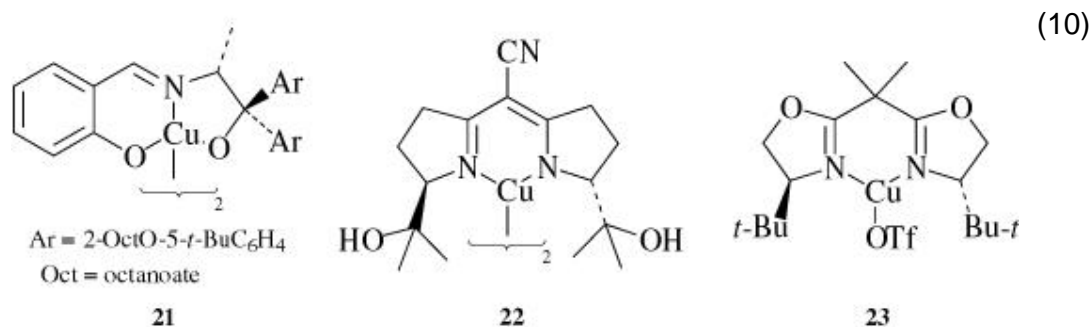
3.2.3. Asymmetric Induction Using Chiral Catalysis

The development of chiral catalysis for asymmetric carbenoid cyclopropanations is of considerable mechanistic and synthetic significance. The observation by Nozaki and co-workers (113, 114) of low enantioselectivity in the reaction of ethyl diazoacetate with styrene catalyzed by copper catalyst 20 (Eq. 9) is a landmark study because it demonstrates that the carbene is associated with the copper catalyst during the cyclopropanation step.

The first report of a highly enantioselective cyclopropanation was described by Aratani using the copper catalyst **21** (Eq. 10). (112, 115-117) In these studies, the highest asymmetric induction was obtained using menthyl esters. Even though the menthyl ester with an achiral catalyst results in low asymmetric induction, its reaction with **21** results in considerable improvement in both enantioselectivity and diastereoselectivity compared to ethyl diazoacetate.

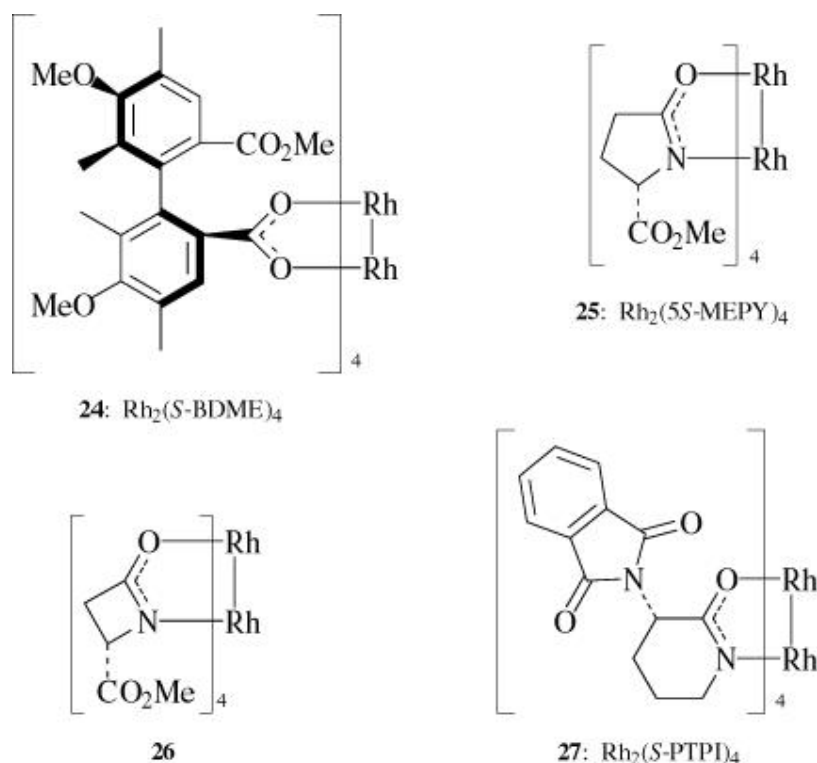


R	catalyst	$E:Z$	% ee (E)	% ee (Z)
O-menthyl- <i>l</i>	21	2.6:1	90	59
O-menthyl- <i>l</i>	22	4.6:1	97	95
BHT	23	15.7:1	99	—

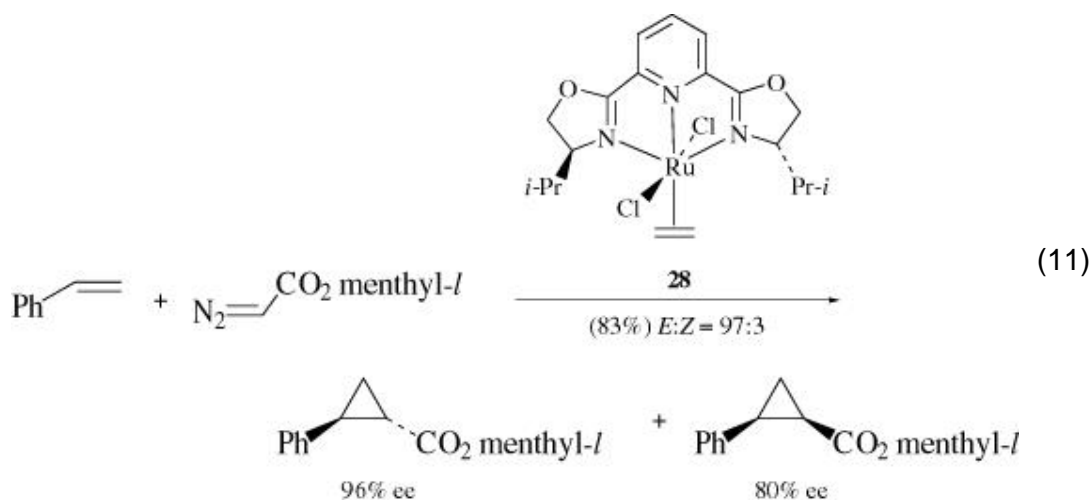


The improved stereoselectivity is primarily due to the increased size of the ester, since the double stereoselection that is observed in this system is rather moderate. The next major breakthrough in this area was the discovery by Pfaltz that C₂ symmetric semicorrin copper complexes **22** are superb catalysts for asymmetric induction. (69, 118-123) Since then, several groups have developed various C₂ symmetric copper catalysts for asymmetric induction. The catalyst that has enjoyed the most general use to date is the bisoxazoline catalyst **23**, developed by Evans and Masamune. (124-126)

As rhodium catalysis tends to result in much cleaner reactions than copper systems, several groups have explored the use of various chiral rhodium complexes for asymmetric cyclopropanation. (3, 29, 30, 49) Dirhodium(II) tetracarboxylates have been generally unsuccessful in asymmetric intermolecular cyclopropanations by diazoacetates, (127, 128) but recently very promising results were achieved with the biphenylcarboxylate catalyst $\text{Rh}_2(\text{S-BDME})_4$ (24). (129) In contrast, various rhodium(II) amide catalysts have been used in intermolecular cyclopropanations with high asymmetric induction. The $\text{Rh}_2(\text{S-MEPY})_4$ catalyst (25), developed by Doyle, was the first catalyst that was shown to result in reasonably high enantioselectivity in intermolecular cyclopropanation, but since then other catalysts such as 26 and 27 have been found that result in even higher enantioselectivity. In all of these systems, a bulky diazoacetate results in higher enantioselectivity than ethyl diazoacetate.

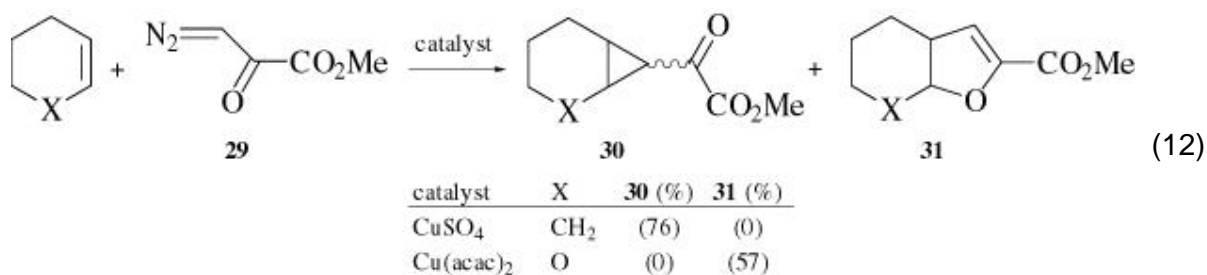


The recent development of the C_2 symmetric ruthenium catalyst 28 for asymmetric cyclopropanation offers one major advantage over both rhodium and copper catalysts because high enantioselectivity and diastereoselectivity can be obtained with this system without resorting to using extremely bulky ester derivatives. (103, 104, 106, 107) Illustrative examples are shown in Eq. 11.

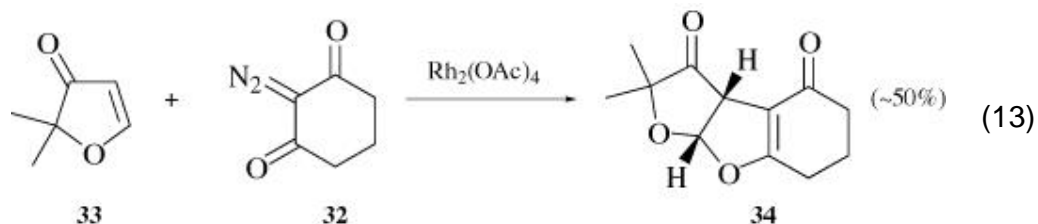


3.3. Carbenoids Derived from Diazoacetates, Diazomalonates, and Related Systems

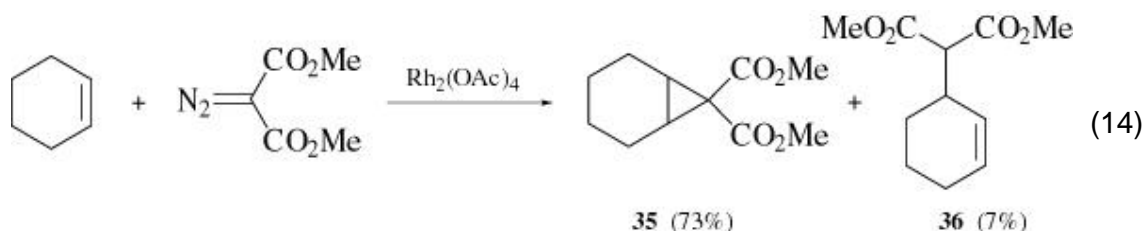
Metal-carbenoid intermediates flanked by two electron-withdrawing groups are highly electrophilic systems. Furthermore, because of their ability to stabilize a negative charge at the carbenoid carbon, products derived from zwitterionic intermediates are commonly observed, especially when the reaction is carried out with electron-rich alkenes. (65, 67, 72, 130-136) Similar chemistry occurs with carbenoids derived from diazopyruvates. (72, 137) Reaction of **29** with cyclohexene results in the formation of the cyclopropane **30**, whereas reaction with dihydropyran forms the fused dihydrofuran **31** (Eq. 12).



The carbenoid derived from 2-diazo-1,3-cyclohexanedione (**32**) is highly susceptible to [3 + 2] annulation chemistry. (67, 136, 138, 139) An illustrative example is the reaction of **32** with dihydrofuranone **33** that results in the formation of the tricyclic system **34** (Eq. 13). (136)

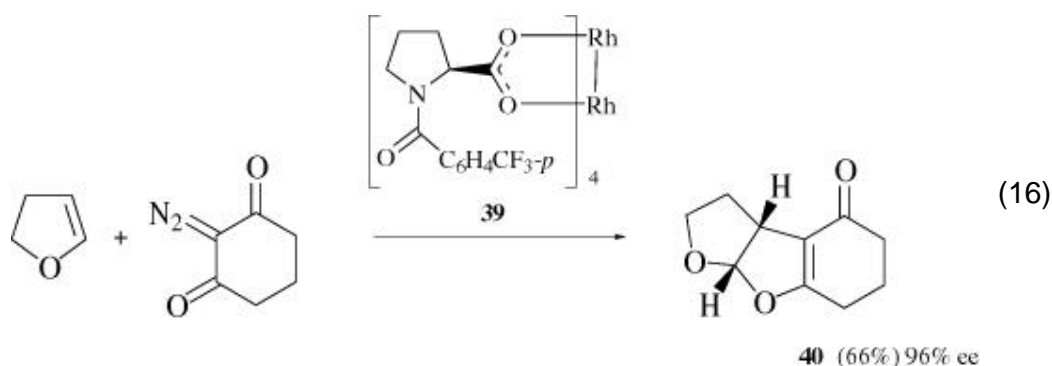
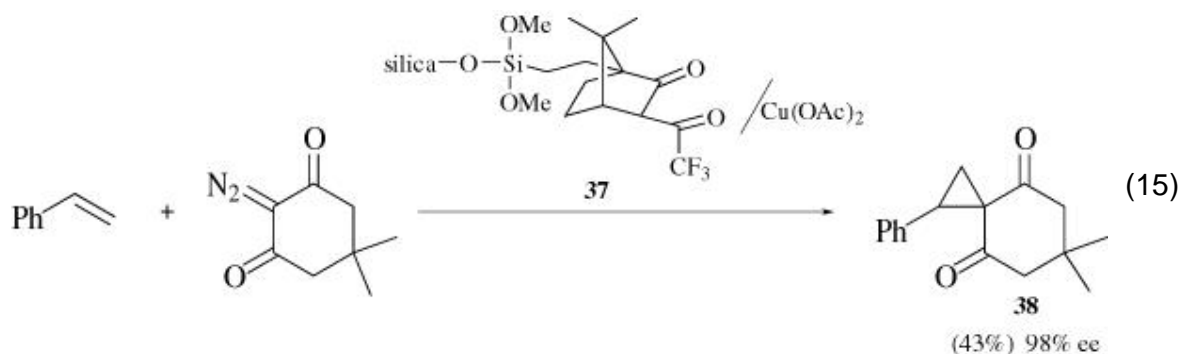


A second side-reaction that is commonly seen with this class of carbenoid intermediates is C-H insertion. (61, 140) Reaction of dimethyl diazomalonate with cyclohexene generates a mixture of the cyclopropane **35** and the C-H insertion product **36** (Eq. 14). In more functionalized cyclohexenes, the C-H insertion can become the dominant reaction pathway. The C-H insertion product could be derived either by a direct C-H insertion mechanism or through proton exchange from a zwitterionic intermediate that could be directly formed on reaction of the carbenoid with the alkene.



3.3.1. Asymmetric Induction

The standard asymmetric protocols that have been developed for the diazoacetate system have not been generally used with the other carbenoid systems. However, two reports described highly enantioselective transformations with the 2-diazo-1,3-cyclohexanedione system. A communication with limited details described highly asymmetric cyclopropanations with the copper catalyst **37** leading to the spirocyclopropane **38** in 98% ee (Eq. 15). (141) A recent report described highly enantioselective [3 + 2] annulations using the rhodium proline catalyst **39** leading to the tricyclic system **40** in 96% ee (Eq. 16). (142)



Both of these reactions represent most unusual cases of asymmetric induction because as the faces of the carbenoid are not enantiotopic, the enantioselectivity must be due to alkene face selectivity. This indicates that the trajectory of alkene approach in the 2-diazo-1,3-cyclohexanedione system must be very demanding, although no detailed model has been proposed to explain the enantioselectivity observed in this system.

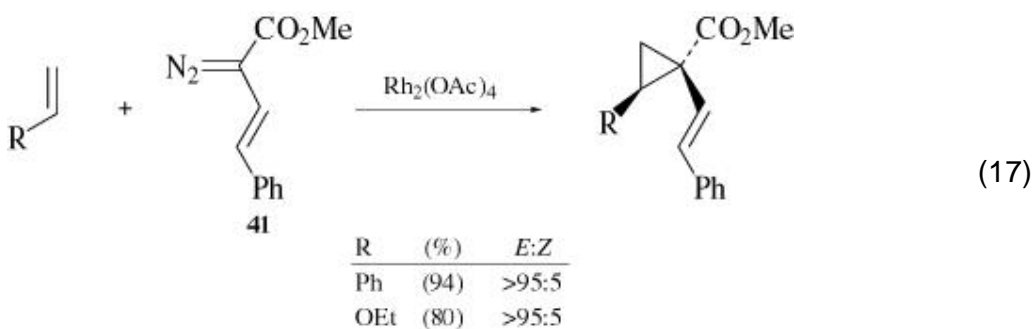
3.4. Carbenoids Derived from Vinyl diazoacetates, Phenyldiazoacetates, and Related Systems

In recent years, it has become clear that carbenoids derived from vinyl diazoacetates have a very different reactivity profile to carbenoids derived from diazoacetates. (4, 6, 7) Intermolecular cyclopropanations will only occur with monosubstituted alkenes, 1,1-disubstituted alkenes, and *cis*-1,2-disubstituted alkenes. (58) Furthermore, many of these reactions are highly diastereoselective, again differing from the typical results obtained with the diazoacetate system.

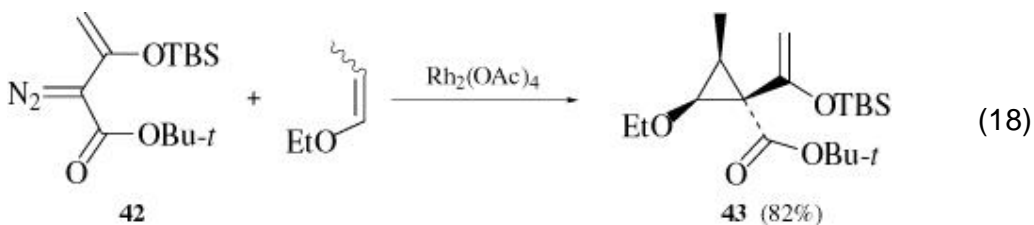
3.4.1. Diastereoselectivity

Cyclopropanations with vinyl diazoacetate **41** are generally highly diastereoselective. (59, 143) The highest diastereoselectivity is obtained with electron-rich alkenes, such as styrene and vinyl ethers, and with vinyl carbenoids lacking an electron-withdrawing group on the vinyl portion (Eq.

17). (59, 143) In many of these reactions, the second diastereomer cannot be observed in the NMR spectrum of the crude reaction mixtures.

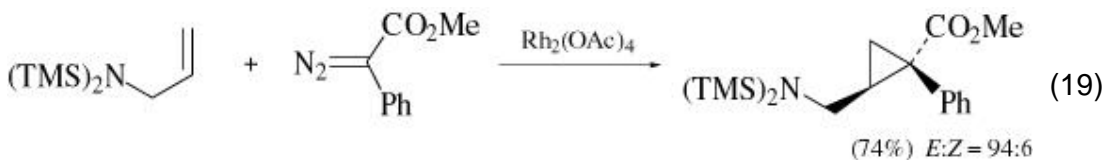


Spectacular chemoselectivity and diastereoselectivity were demonstrated during a short synthesis of the ether analog of acetomycin (Eq. 18). (144) Decomposition of the vinyl diazoacetate **42** in the presence of an *E/Z* mixture of ethyl 1-propenyl ether results in the formation of **43**, containing three stereogenic centers, as a single diastereomer.



Only the *Z* vinyl ether is capable of reacting with the carbenoid, and the high diastereoselectivity typical of the vinyl diazoacetate system is obtained.

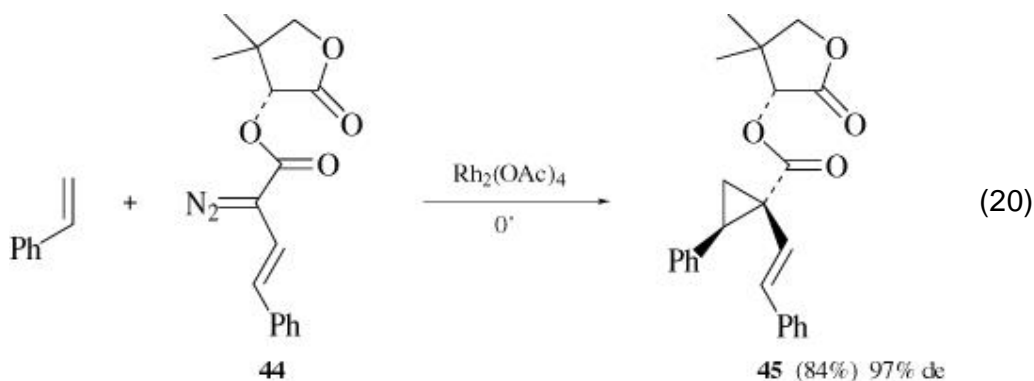
Similar highly diastereoselective cyclopropanations have been reported for the phenyldiazoacetate system, as illustrated in Eq. 19. (73, 74, 145, 146)



A comparison study of a range of carbenoid systems concludes that these highly diastereoselective cyclopropanations occur only in the case of carbenoids that are flanked by both an electron-withdrawing group and an electron-releasing group such as vinyl or phenyl. (73)

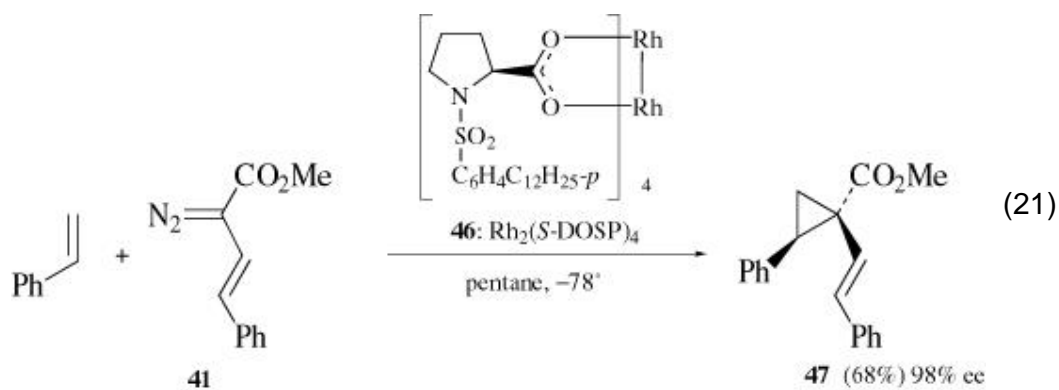
3.4.2. Asymmetric Induction Using Chiral Auxiliaries

In contrast to the results in the diazoacetate system, chiral auxiliaries have been found to be very effective in asymmetric vinyldiazoacetate cyclopropanations. (147, 148) Inexpensive α -hydroxy esters are excellent chiral auxiliaries for these transformations. The highest asymmetric induction is obtained using (*R*)-pantolactone as the chiral auxiliary, as illustrated for the reaction of the vinyldiazoacetate **44** with styrene, which results in the formation of vinylcyclopropane **45** in 97% diastereomeric excess (de) (Eq. 20). (148) An even less expensive, effective chiral auxiliary is methyl (*S*)-lactate, although in general the asymmetric induction observed is lower than that achieved using (*R*)-pantolactone. (148)



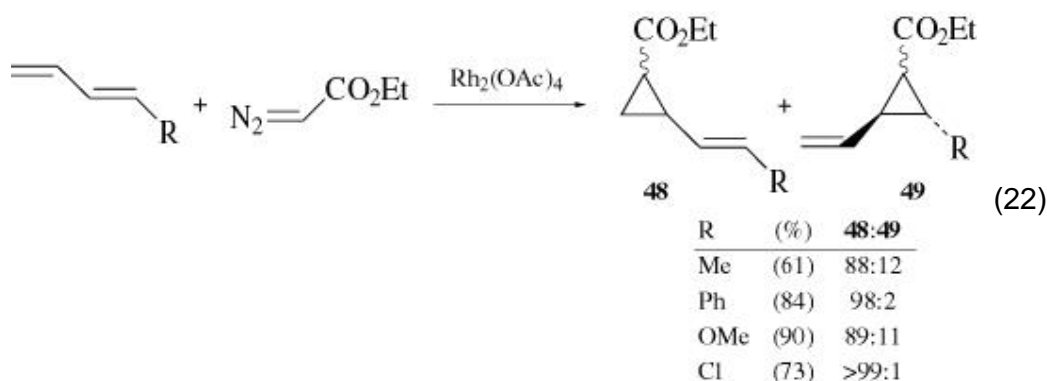
3.4.3. Asymmetric Induction Using Chiral Catalysts

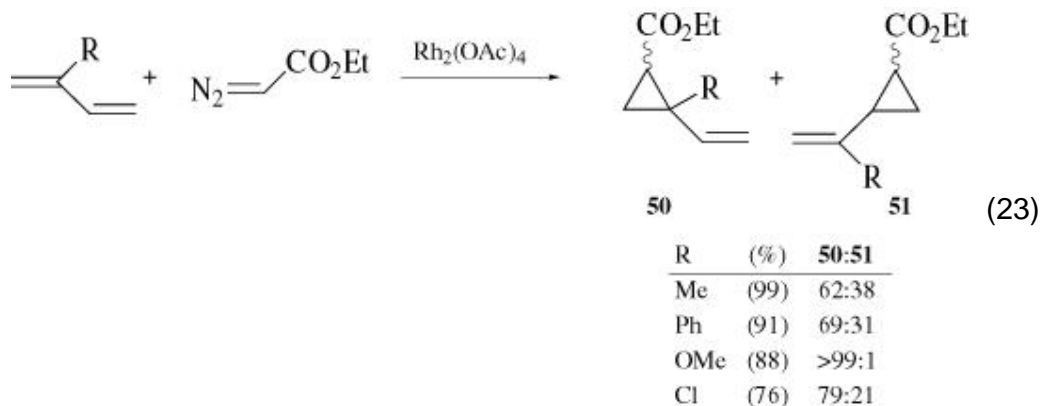
Although rhodium (II) prolinates are poor chiral catalysts for diazoacetate cyclopropanations, they are extremely effective for asymmetric cyclopropanations with vinyldiazoacetates. (5, 58, 128) The highest degrees of asymmetric induction are obtained when the reactions are carried out in nonpolar solvents at low temperatures. Consequently, the most effective catalyst to date is $\text{Rh}_2(\text{S-DOSP})_4$ (**46**) which is soluble in pentane even at -78° . $\text{Rh}_2(\text{S-DOSP})_4$ -catalyzed decomposition of the vinyldiazoacetate **41** in the presence of styrene at -78° results in the formation of cyclopropane **47** in 98% ee (Eq. 21). (58)



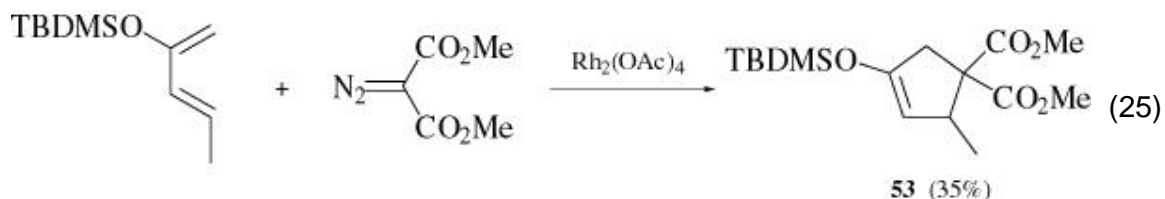
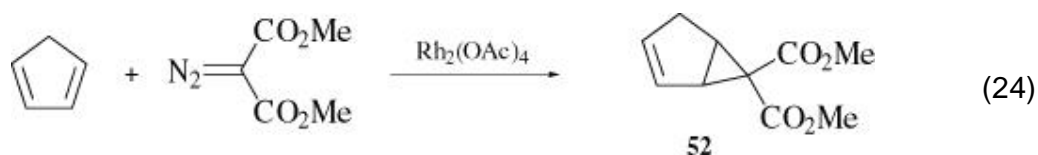
3.5. Cyclopropanation of Dienes

The reaction of diazo compounds with dienes is a useful synthetic process because the resulting vinylcyclopropanes can be used in further synthetic transformations. (149) The reaction with dienes offers an interesting test of regioselectivity wherein the two double bonds compete for the active carbenoid intermediate. Several systematic studies on the reaction of ethyl diazoacetate with 1-substituted dienes and 2-substituted dienes demonstrate that reasonable selectivity between the double bonds can be achieved in appropriately substituted dienes. (150, 151) In 1-substituted dienes, a chloro substituent gives the highest regiochemistry (48:49, Eq. 22) favoring the sterically less crowded double bond, (151) whereas in 2-substituted dienes, a methoxy substituent gives the highest regioselectivity (50:51, Eq. 23). (151) As is typical of diazoacetate cyclopropanations, low diastereoselectivity is obtained in these reactions.





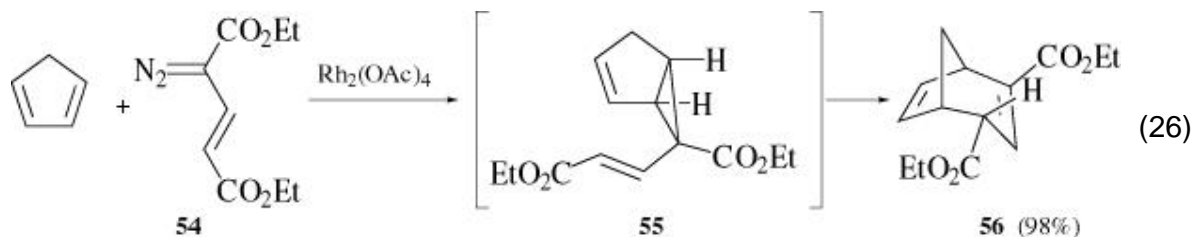
The reaction of dimethyl diazomalonate with dienes can lead either to cyclopropanation (Eq. 24) (152) or to [4 + 1] cycloaddition (Eq. 25). (53)



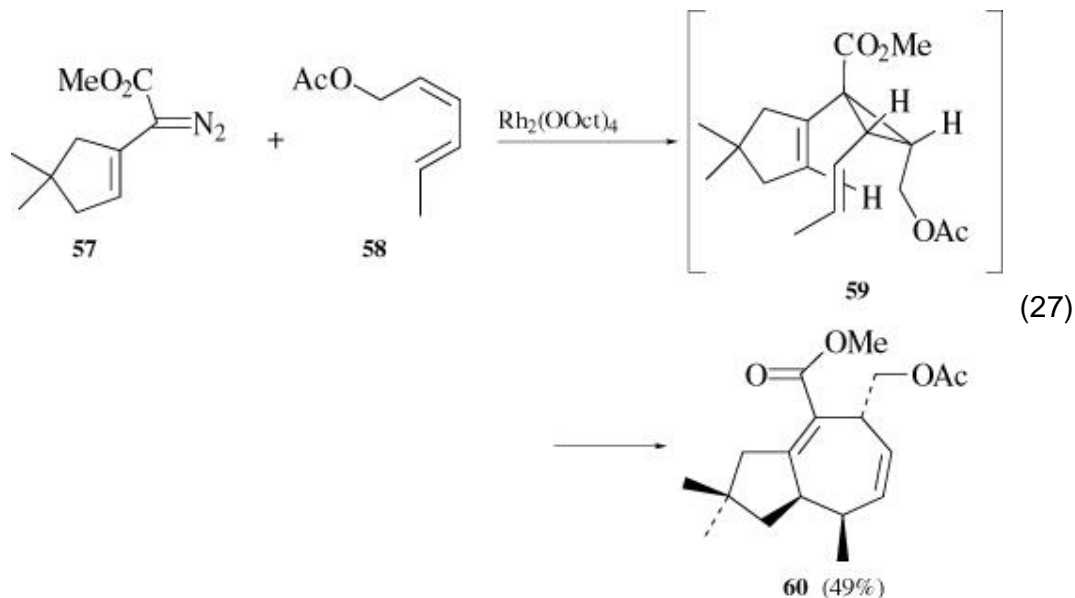
The outcome of this chemistry is dependent on the electronic structure of the diene. Unpolarized dienes tend to form cyclopropanation products (52), whereas electron-rich dienes tend to form the [4 + 1] annulation products (53). The [4 + 1] annulation products may be derived from zwitterionic intermediates, although it has been postulated that a metallocyclohexene intermediate may be involved in these reactions. (53)

The reaction of vinylcarbenoids with dienes leads to the formation of *cis*-divinylcyclopropanes. (4, 7) Cyclopropanations with vinyl diazoacetates are highly diastereoselective, and in most instances no evidence for the formation of the *trans*-divinylcyclopropanes is observed. As *cis*-divinylcyclopropanes undergo a Cope rearrangement under mild conditions, (153, 154) the combined cyclopropanation/Cope rearrangement is a very direct method for the synthesis of cycloheptadienes of defined stereochemistry. Most effective in

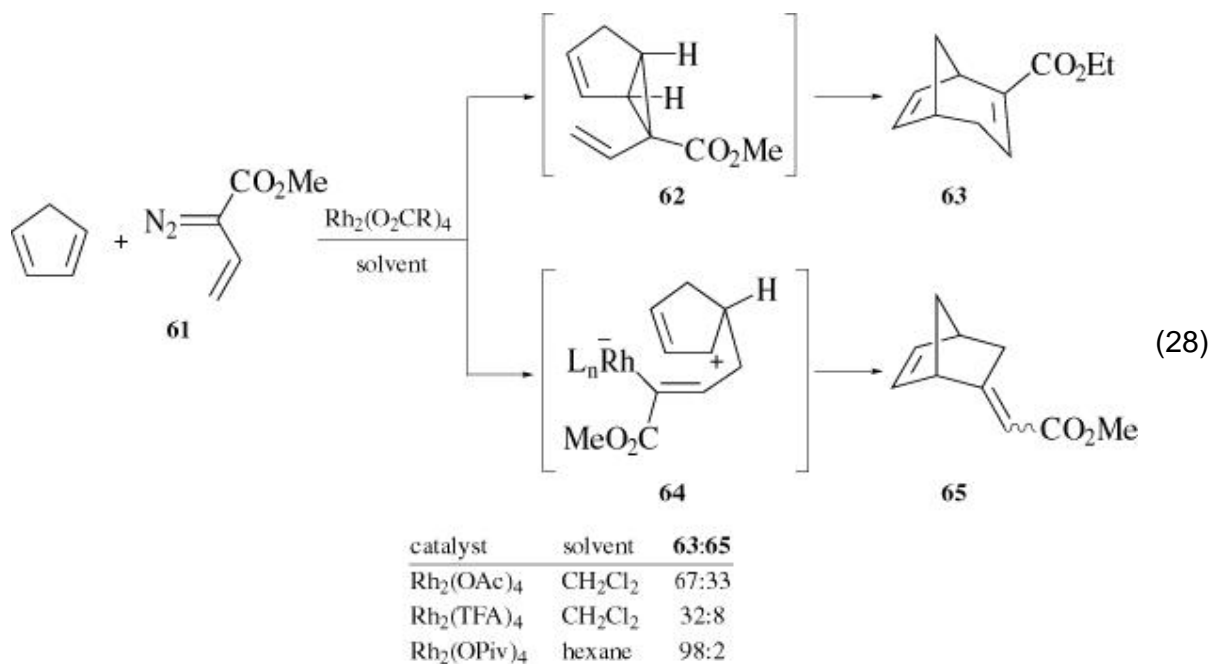
this regard is the reaction of vinyl-diazoacetates with dienes, because in most instances the cyclopropanation is highly diastereoselective and the resulting *cis*-divinylcyclopropanes rearrange to cycloheptadienes under the reaction conditions. (4, 7) An illustrative example is the reaction of vinyl diazoacetate **54** with cyclopentadiene that results in the formation of the *endo*-bicyclooctadiene **56** in 98% yield. (155, 156) The stereoselective nature of this reaction is attributable to the requirement for a boat-like transition state for the rearrangement of the *cis*-divinylcyclopropane **55**.



A further notable feature of vinyl diazoacetate reactions is that the carbenoid is very sensitive to both steric and electronic effects, which leads to the possibility of highly regioselective cyclopropanations with unsymmetrical dienes. (156, 157) An example of this phenomenon is seen in the key annulation step in the synthesis of tremulenolide A. (158) Reaction of **57** with the (*E/Z*)-diene **58** results in the formation of a single [3 + 4] annulation product **60** in 49% yield. Even though the diene is not electronically biased, carbenoids derived from vinyl diazoacetates do not undergo intermolecular cyclopropanation with *trans* alkenes. Consequently, the *cis* double bond in **58** is selectively cyclopropanated leading to *cis*-divinylcyclopropane **59**, which rearranges through a boat-like transition state to **60**.



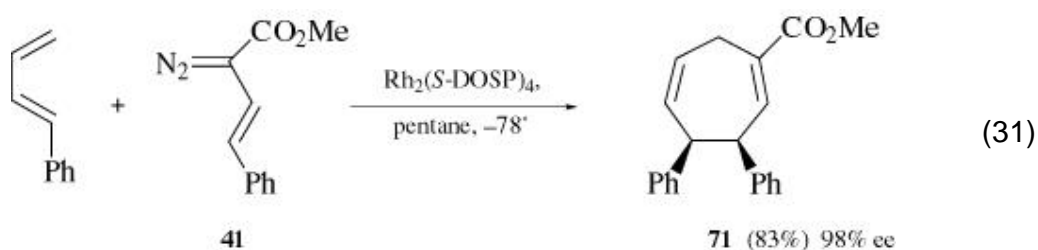
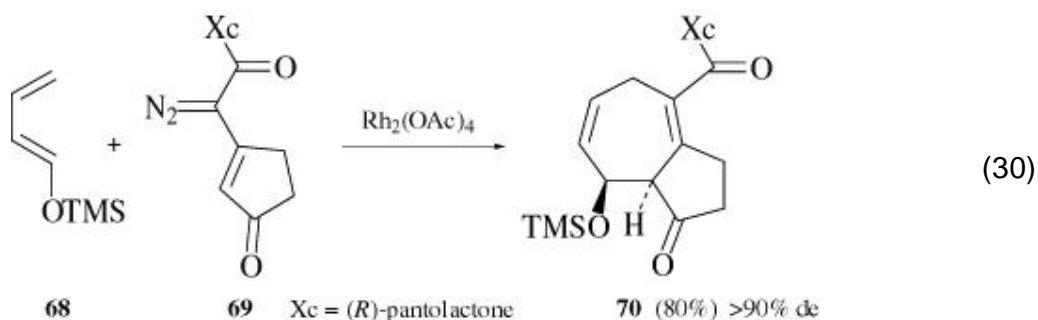
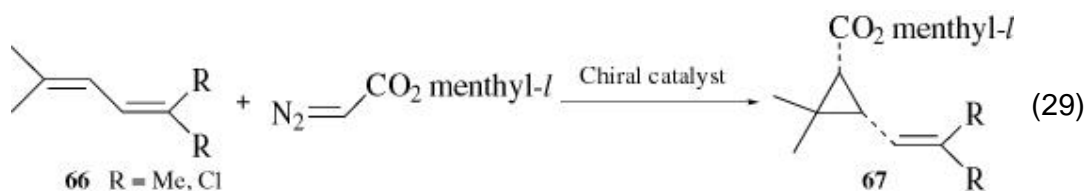
An unusual side-reaction occurs with vinylcarbenoids derived from **61** that lack a substituent on the vinyl terminus, as seen in Eq. 28. (159) In addition to the [3 + 4] annulation product **63**, the bicyclo[2.2.1] system **65** is formed.



This system is considered to be formed by reaction of the vinylcarbenoid at the vinylogous position instead of at the carbenoid center leading to zwitterionic intermediate **64** instead of divinylcyclopropane **62**. Use of a combination of

relatively electron-rich catalysts, such as dirhodium tetrapivalate, and nonpolar solvents can circumvent the reactivity at the vinylogous position.

Both the chiral auxiliary and catalyst approaches have been effectively used for asymmetric cyclopropanation of dienes. A commercially important transformation is the reaction of menthyl diazoacetate with **66** to form the vinylcyclopropanes **67**, important intermediates in the synthesis of pyrethroids (Eq. 29). The reaction of chiral vinyl diazoacetates with dienes can occur with high asymmetric induction as illustrated in Eqs. 30 (148) and 31. (157)

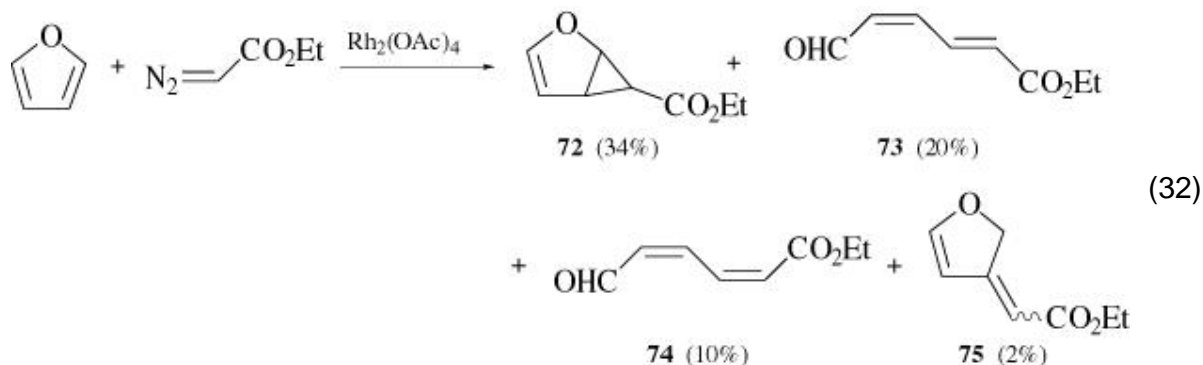


Reaction of **68** with diene **69** results in the formation of the bicyclic system **70** in greater than 90% de. $\text{Rh}_2(\text{S-DOSP})$ -catalyzed decomposition of vinyl diazoacetate **41** in the presence of *trans*-1-phenyl-1,3-butadiene results in the formation of the *cis*-diphenylcyclo-heptadiene **71** in 98% ee.

3.6. Reactions of Carbenoids with Furans

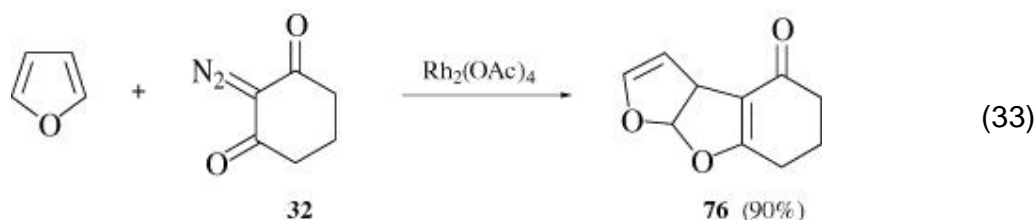
The reaction of carbenoids with furans usually leads to the unraveling of the heterocycle resulting in the formation of differentially functionalized dienes in good yield. (54, 160-171) A re-examination of the reaction between ethyl

diazoacetate and furan revealed the formation of four products, furanocyclopropane **72**, two isomeric dienes **73** and **74**, and a trace of alkylated product **75** in 66% overall yield (Eq. 32). (172, 173)



The furanocyclopropane **72** is unstable, however, and on prolonged standing or on treatment with iodine rearranges cleanly to the *Z,E* diene **73**. Furans with electron-withdrawing groups such as esters (172, 173) and unsaturated esters (172, 173) can participate in this chemistry, but competing cyclopropanation of the vinyl group occurs with vinylfurans. (174)

The reaction of 2-diazo-1,3-cyclohexanedione (**32**) with furans results in the formation of [3 + 2] annulation products such as **76** (Eq. 33). (67)

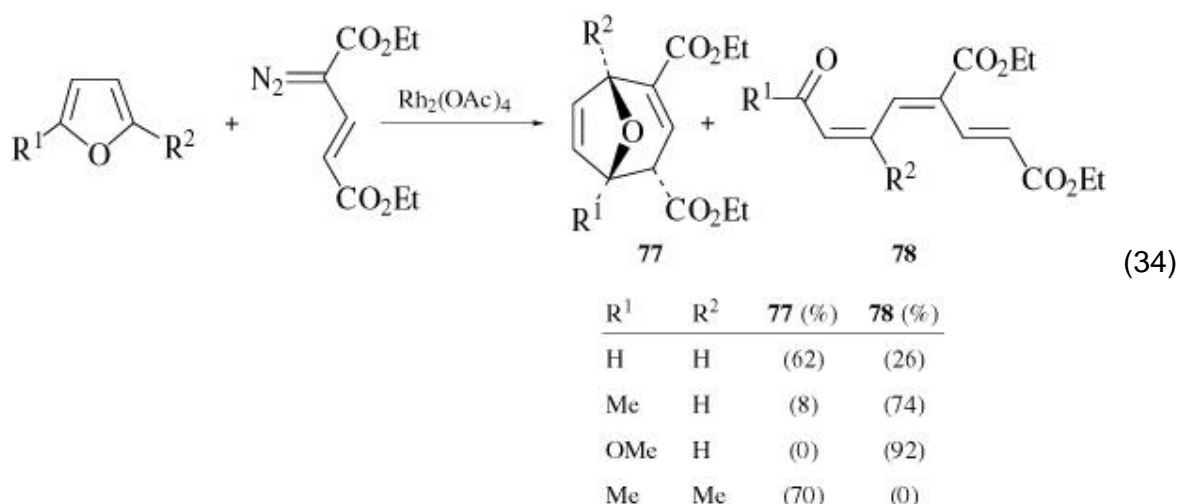


The regiochemistry of these reactions is most puzzling because they would involve the intermediacy of the less stabilized of the two possible zwitterionic intermediates. A mechanism has been proposed in which the reaction proceeds by an initial cyclopropanation, which is then followed by selective ring opening to the zwitterionic intermediate. (67) Alternatively, it has been suggested that the zwitterionic intermediate is directly formed, and the regiochemistry is controlled by steric factors that govern the approach of the furan to the carbenoid. (175) Limited attempts have been made to achieve asymmetric induction in this reaction using a dirhodium tetra(binaphthylphosphate) catalyst. (176)

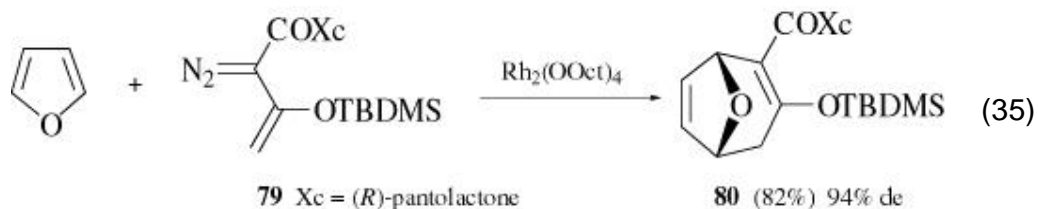
Reactions of vinylcarbenoids with furans offer another level of complexity because the furanocyclopropanes in these cases would be

divinylcyclopropanes capable of Cope rearrangement in addition to electrocyclic ring opening to trienes. (166, 167) As illustrated in Eq. 34, the product distribution is very dependent on furan structure. With 2,5-disubstituted furans, bicyclo[3.2.1] systems **77** are formed exclusively, but with furan or 2-substituted furans, trienes **78** are also produced. In these reactions, the trienes are considered to be derived from zwitterionic intermediates arising from attack of the carbenoid at the α -position of the furan, whereas the furanocyclopropanes cleanly rearrange to **77**.

Asymmetric [3 + 4] annulations between vinylcarbenoids and furans are readily achieved using chiral auxiliaries, as demonstrated in the asymmetric synthesis of 8-oxabicyclo[3.2.1]octan-3-ones. (177)

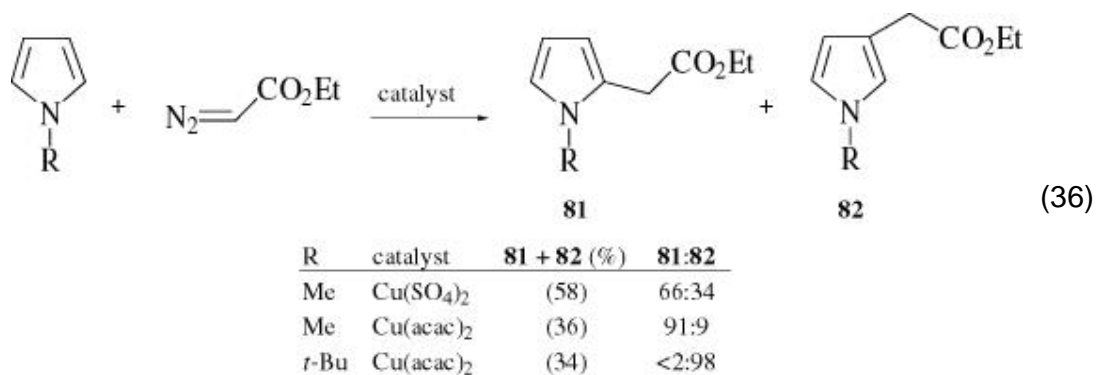


These oxabicyclic systems are very versatile intermediates for organic synthesis but typically they have been prepared in racemic form by the [3 + 4] annulation between allyl cations and furans. (178) An illustrative example is the reaction of siloxyvinyl diazoacetate **79** with furan, which generates the 8-oxabicyclo[3.2.1]octadiene **80** in 82% yield and 94% de (Eq. 35). (177)



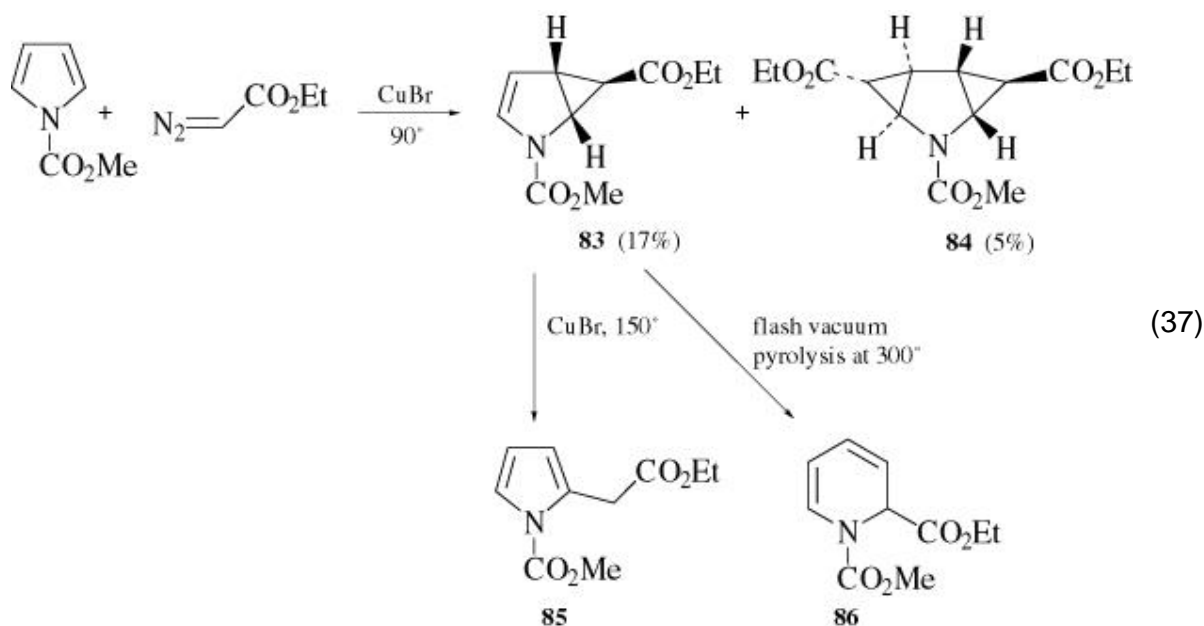
3.7. Reactions of Carbenoids with Pyrroles

The reaction of carbenoids with pyrroles commonly leads to either substitution or cyclopropanation products, depending on the functionality on nitrogen. (179) The reaction with *N*-alkylated pyrroles leads exclusively to substitution products. In view of the pharmaceutical importance of certain pyrrolylacetates, the reaction of alkyl diazoacetates with pyrrole has been extensively studied. (66, 180, 181) Both the 2- and 3-alkylated products, **81** and **82**, can be formed; the ratio is dependent on the catalysts and the size of the *N*-alkyl and ester groups.



Some illustrative examples of the trends that are observed are shown in Eq. 36. (180) This has been interpreted as evidence that transient cyclopropane intermediates are not involved in this reaction because if this were the case the catalyst should not have influenced the isomer distribution. Instead, the reaction is believed to proceed by dipolar intermediates, whereby product control is determined by the position of electrophilic attack by the carbenoid.

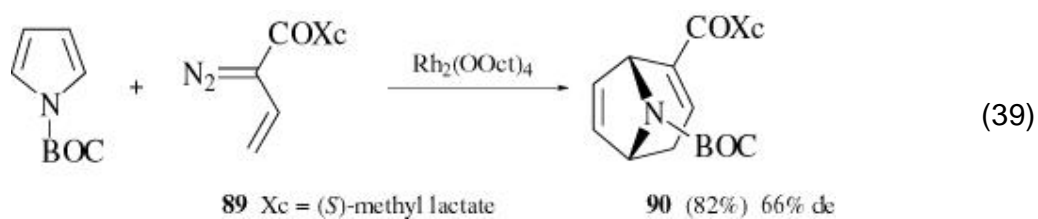
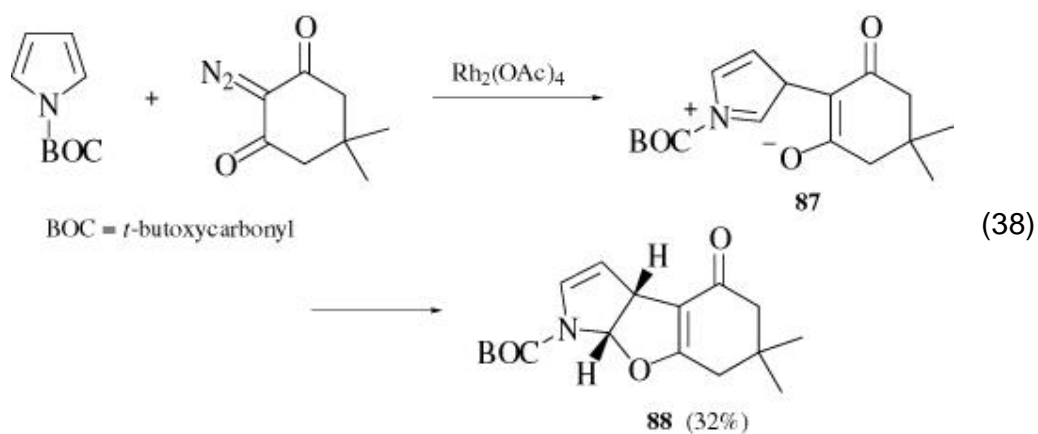
The reaction of ethyl diazoacetate with *N*-acylated pyrroles in the presence of cuprous bromide generates the 2-azabicyclo[3.1.0]hex-3-ene system **83** and some of the diadduct **84** (Eq. 37). (182) Higher yields of **83** can be obtained by using Rh₂(OAc)₄. (183)



Heating of **83** in the presence of cuprous bromide causes rearrangement of **83** to the 2-pyrrolylacetate **85**, which is considered to arise from a zwitterionic intermediate. In contrast, on flash vacuum pyrolysis **83** is transformed to dihydropyridine **86**. A plausible mechanism for the formation of **86** is the rearrangement of **83** to an acyclic dieneimine analogous to the furan ring opening, which then undergoes a 6π electrocyclicization to **86**.

In a manner analogous to furan cycloadditions as illustrated in Eq. 33, the reaction of diazodimedone with *N*-BOC-pyrrole results in an intriguing [3 + 2] annulation product **88** (Eq. 38). (67) The regiochemistry would require the formation of zwitterionic intermediate **87** where the carbenoid is attached to the 3-position of the pyrrole. It has been suggested that the preferential formation of **87** rather than the more stable 2-substituted zwitterionic structure is due to either the regio-chemistry of ring opening of the pyrrolocyclopropane (67) or the steric demands for approach of the carbenoid to the pyrrole. (175)

The reaction between vinylcarbenoids and pyrroles is a general method for the stereoselective construction of tropanes (Eq. 39). (184, 185) Side-reactions due to vinyl terminus reactivity occur with vinylcarbenoids lacking functionality at the vinyl terminus, but this reactivity can generally be avoided by using nonpolar solvents. (185)

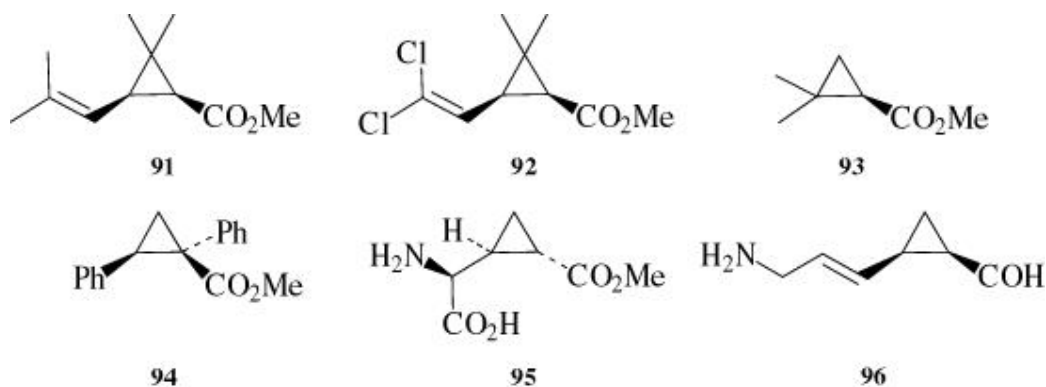


Asymmetric reactions using a chiral catalyst such as $\text{Rh}_2(\text{S-TBSP})_4$ are not particularly effective in this case because the pyrrole is too electron-rich and leads to products derived from zwitterionic intermediates in addition to tropanes. (175) The asymmetric synthesis of tropanes, however, can be achieved by reaction of *S*-lactate derivatives like **89** with *N*-BOC-pyrrole, leading to tropanes such as **90** with respectable yields and diastereoselectivity. (175, 186) The sense of asymmetric induction using α -hydroxy esters as chiral auxiliaries is opposite on going from furans (177) to pyrroles. (175) This has been explained as a change in facial selectivity on the heterocycle during non-synchronous cyclopropanation with predominant initial bond formation on furan occurring at the 2-position, and on *N*-BOC-pyrrole at the 3-position.

4. Synthetic Utility

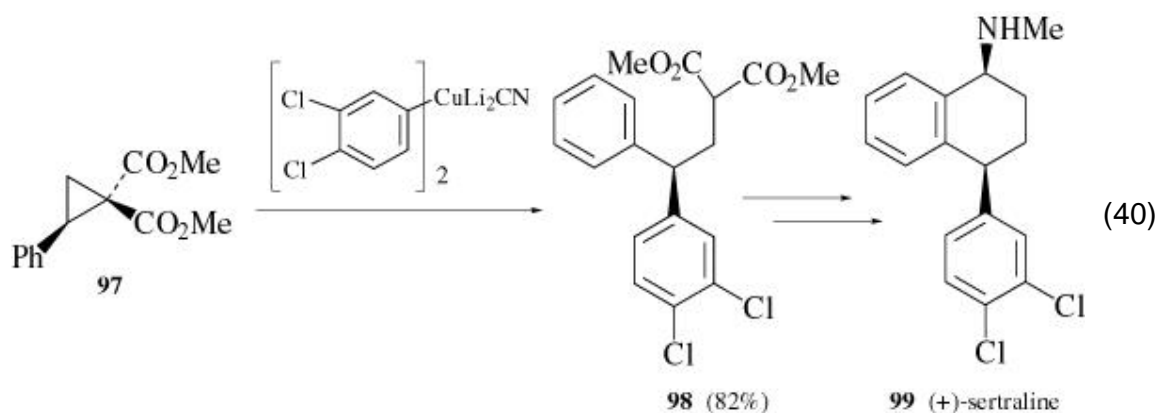
The stereoselective synthesis of cyclopropanes is a transformation of considerable importance. The cyclopropane unit is present in a number of natural and commercial products. (187, 188) Furthermore, a number of stereoselective ring opening and ring expansion reactions of cyclopropanes have been developed into versatile synthetic methods. (149, 153, 154, 189-193) As can be seen from this chapter, the metalcatalyzed decomposition of diazo compounds in the presence of alkenes is an extremely general method for the synthesis of cyclopropanes. With the development of a range of excellent chiral catalysts, the majority of these cyclopropanations can, in principle, be achieved with high asymmetric induction. The diastereoselectivity in these cyclopropanations has been difficult to control but major improvements have now been made since the understanding of the effect of carbenoid structure (59, 78) and catalysts (78, 99, 106) on diastereoselectivity has improved.

The early commercial interest in devising catalysts for asymmetric cyclopropanation was directed primarily toward the asymmetric synthesis of pyrethroids, (194) such as chrysanthemic acid **91** and permethrinic acid **92**. Similarly, the asymmetric cyclopropanation of 2-methylpropene was developed as a direct route to **93**, which is the cyclopropane constituent of the antibiotic cilastatin. (117, 126) Various conformationally constrained cyclopropane amino acids (187, 188) such as **94-96** (58, 195, 196) have also been prepared by intermolecular cyclopropanations.

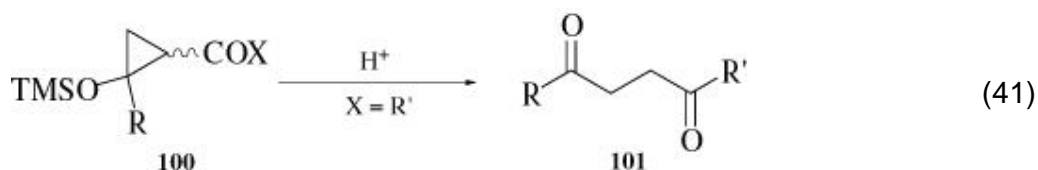


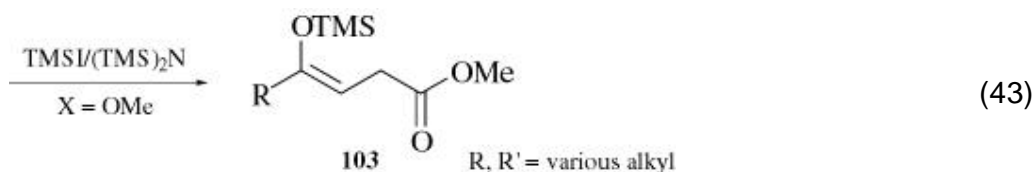
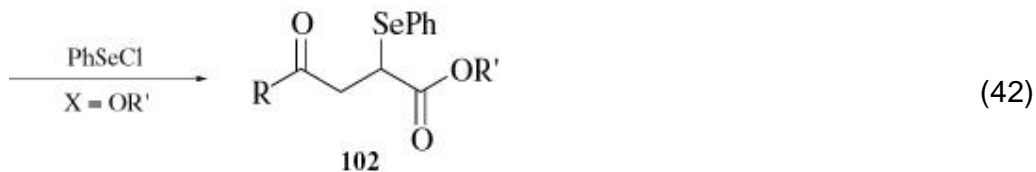
Because of the strain associated with the cyclopropane system, a variety of ring-opening and ring-expansion reactions can occur. These reactions have been extensively reviewed. (149, 153, 154, 189-193) Only a few illustrative examples of the most useful synthetic processes will be described here.

Nucleophile-induced ring-opening of cyclopropanes generally proceeds with inversion of configuration. (190) Only very powerful soft nucleophiles will react with monoactivated cyclopropanes but a much wider range of nucleophiles can be used if two electron-withdrawing groups are present on the cyclopropane. (197, 198) Ring opening of cyclopropanes by nitrogen nucleophiles has been used for the synthesis of alkaloids. (199) An elegant application of cuprate-induced ring opening of cyclopropanes was demonstrated by Corey for the asymmetric synthesis of the antidepressant (+)-sertraline (99). (200) Cuprate-induced ring opening of enantiomerically pure 97 generates the diaryl derivative 98, which is readily converted to (+)-sertraline by a series of standard reactions.



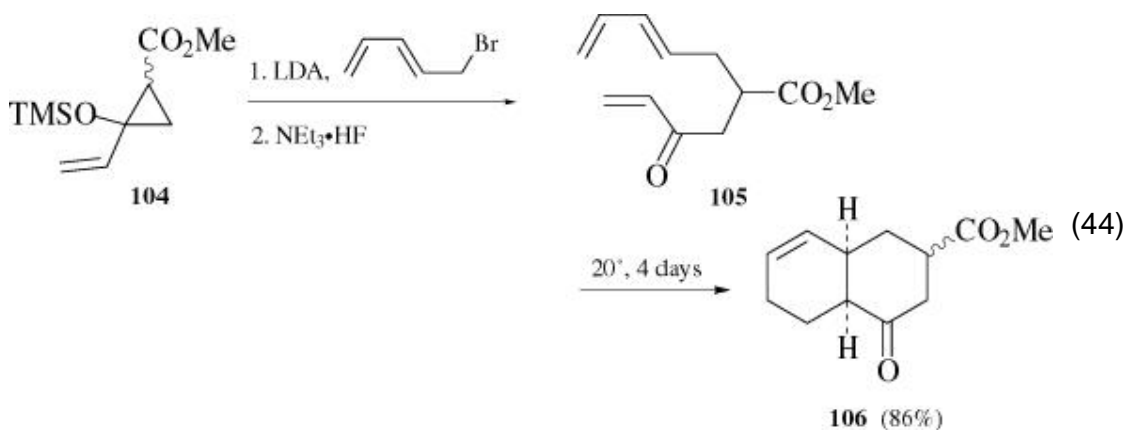
Vinyl ethers are very efficiently cyclopropanated and the resulting donor/acceptor-substituted cyclopropanes (100) have been widely used in organic synthesis. (149, 190) Ring opening can be achieved under very mild conditions resulting in a versatile approach to 1,4-difunctionalized compounds. Illustrative general examples are shown in Eqs. 41, 42, 43. (62)

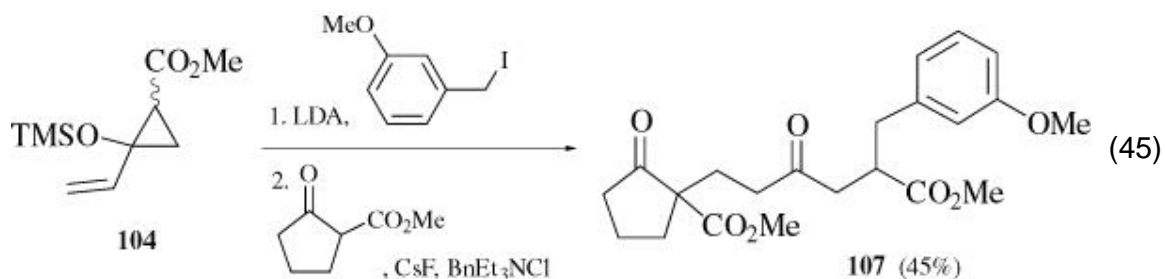




On treatment with mild acid, ring opening of **100** occurs to form 1,4-dicarbonyl compounds **101**, which can be used for the synthesis of cyclopentenones or furans. Alternatively, treatment of **100** with phenylselenenyl chloride generates selenylated products **102**, (201) while treatment with a catalytic amount of trimethylsilyl iodide and bis(trimethylsilyl)amine results in the formation of silylated products **103**. (202)

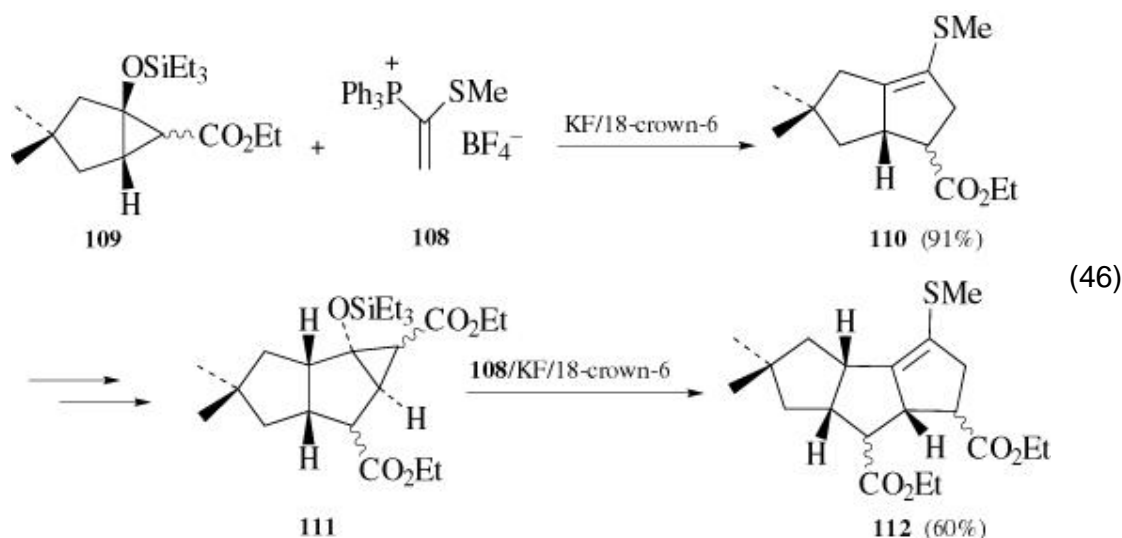
The enolate of the cyclopropane **104** is readily formed, and can undergo aldol reactions or alkylations. (53, 149, 203-208) The resulting aldol products can undergo ring opening to a variety of products such as β , γ -unsaturated ketones, furanones, tetrahydrofurans, dihydrofurans, and macrocycles. (206) Illustrative examples of the synthetic potential of this chemistry are shown in Eqs. 44 (209) and 45. (203) Alkylation of the enolate from **104**, followed by treatment with fluoride, generates the ring-opened product **105**, which on standing undergoes a smooth transformation to the Diels-Alder cycloadduct **106**. (209)





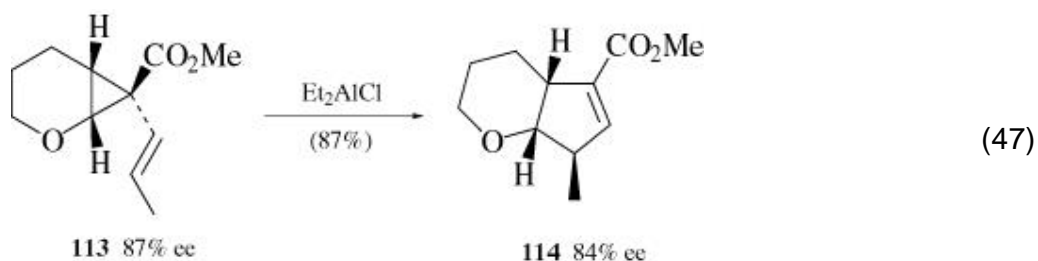
Alternatively, alkylation of the vinylcyclopropane **104** followed by Michael addition-induced ring opening generates **107**, which can be converted to a mixture of steroid products in 56% combined yield. (203)

An elegant strategy for the synthesis of fused cyclopentanoids comprises the reaction between donor/acceptor substituted cyclopropanes and phosphonium salt **108** (Eq. 46). (210, 211) Reaction of **108** with cyclopropane **109** generates bicyclic system **110**. Further conversion of **110** to **111** enables the annulation sequence to be repeated to form triquinane derivatives such as **112**.



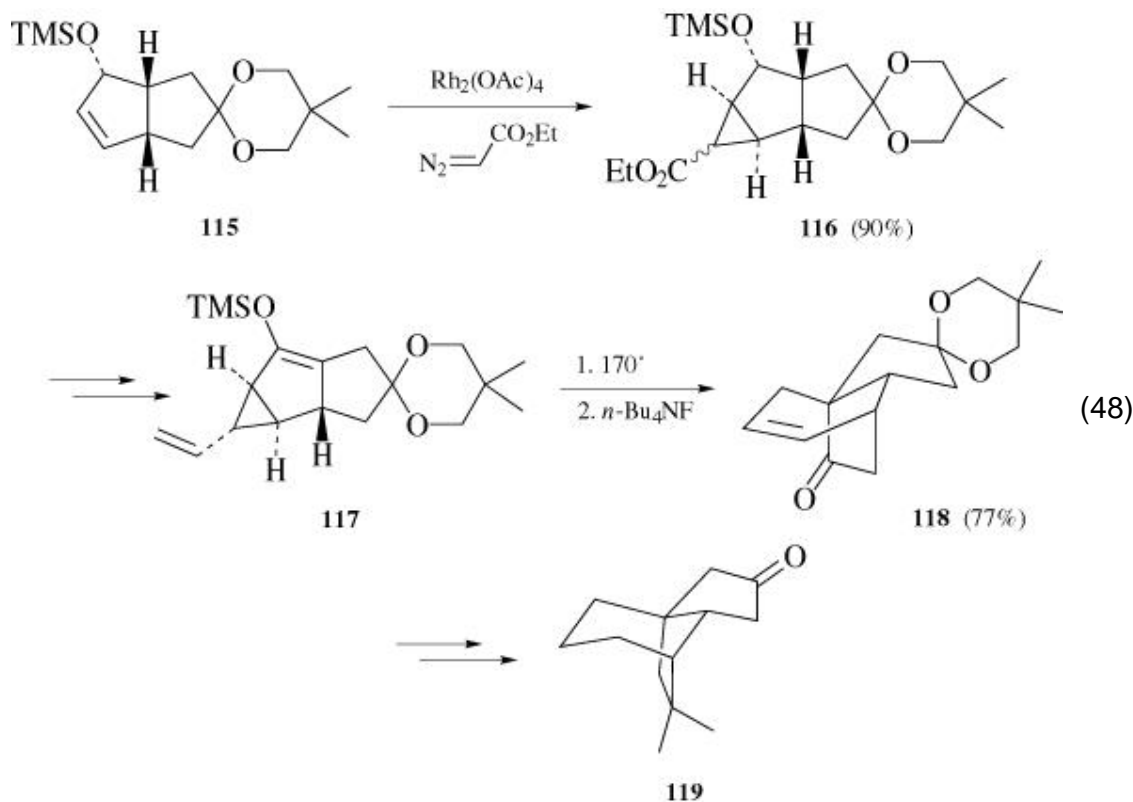
The vinylcyclopropane/cyclopentene rearrangement has been extensively used in organic synthesis. (189) Traditionally, flash vacuum pyrolysis conditions are required to achieve the rearrangement, (189) but when the vinylcyclopropane contains donor and acceptor substituents, mild Lewis acid conditions can be used. (212, 213) The combination of an intramolecular cyclopropanation of a diene followed by rearrangement to a cyclopentene has been used in the total synthesis of several natural products. An example of the

use of a product derived from an intermolecular reaction is shown in Eq. 47. (213)



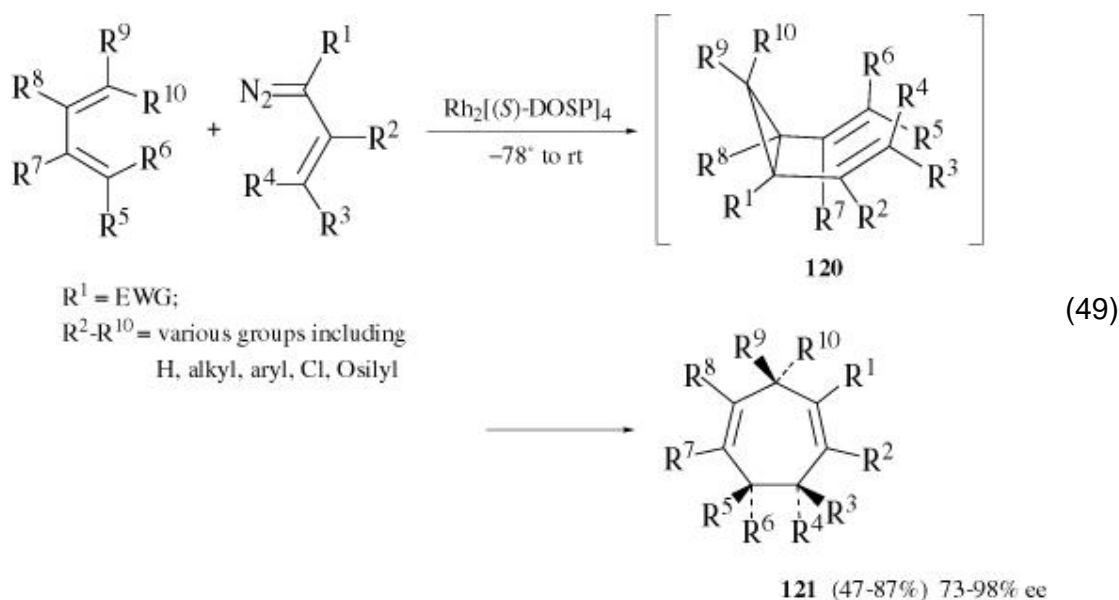
Diethylaluminum chloride catalyzed rearrangement of **113** to cyclopentene **114** occurs with full control of relative stereochemistry.

The Cope rearrangement of *cis*-divinylcyclopropanes is thermally allowed and is a powerful method for the stereoselective synthesis of cycloheptadienes. (7, 153, 154) Divinylcyclopropanes can be prepared from the reaction of ketocarbenoids with dienes followed by methylenation of the keto group. An example of this approach is the formal synthesis of (\pm)-quadron shown in Eq. 48. (214)

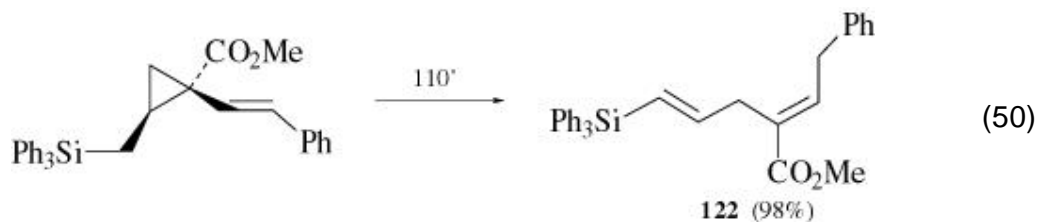


Decomposition of ethyl diazoacetate in the presence of the bicyclic compound **115** results in selective cyclopropanation to form cyclopropane **116**. Further modification of **116** generates the *trans*-divinylcyclopropane **117**, which on thermolysis followed by desilylation produces the tricyclic system **118**. Conversion of **118** to the ketone **119** completes the formal synthesis of (\pm)-quadrone.

A major advance in the use of carbenoids to prepare *cis*-divinylcyclopropanes **120** is the highly diastereoselective reaction between vinyl diazoacetates and dienes. Compounds such as **120** generally rearrange at or below room temperature to the cycloheptadienes **121** with full control of relative stereochemistry (Eq. 49). (4, 7) Furthermore, as chiral auxiliaries and chiral catalysts are very effective for asymmetric vinylcarbenoid cyclopropanations, the enantioselective synthesis of cycloheptadienes is readily achieved. (157) This reaction is applicable to a wide range of dienes including furans (177) and *N*-acylated pyrroles. (175)

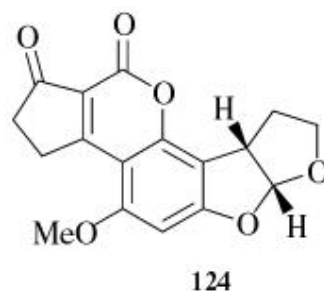
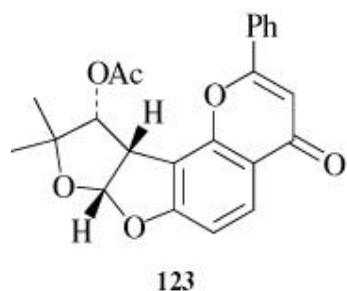


Another useful rearrangement of 2-vinylcyclopropanecarboxylates is the homodienyl rearrangement that leads to the formation of β , γ -unsaturated esters of defined alkene geometry. (193) The illustrative example shown in Eq. 50 leads to the vinylsilane **122**.

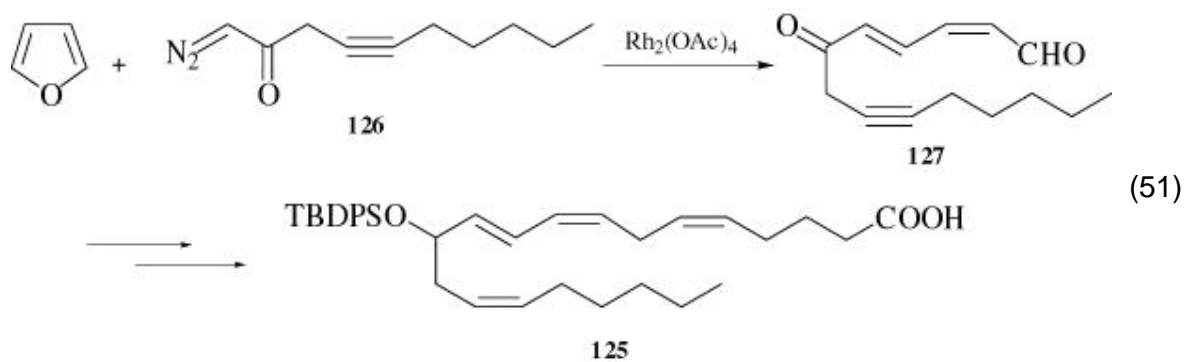


In many instances, the reaction between a carbenoid and an alkene does not lead to the isolation of cyclopropanes. This is especially prevalent when two electron-withdrawing groups are attached to the carbenoid and the alkene is electron-rich. A very useful reaction is the [3 + 2] annulation that occurs on reaction of 2-diazo-1,3-cyclohexanedione with vinyl ethers. This chemistry has been elegantly developed for the construction of natural products, such as (-)-pseudosemiglabrin (**123**) (**136**) and aflatoxin B₂ (**124**). (**215**)

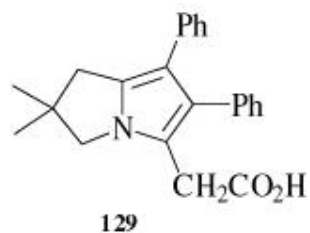
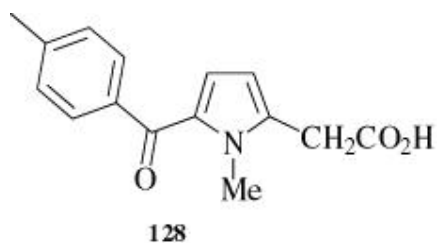
The furan fragmentation that can occur on reaction of carbenoids with dienes is a useful method for the synthesis of *Z,E* dienes.



Numerous applications of this chemistry to the synthesis of leukotrienes have been reported (**163**, **164**, **168**, **169**) as illustrated for the preparation of 12-hydroxyeicosatetraenoic acid (**125**). (**169**) Reaction of the carbenoid precursor **126** with furan in the presence of rhodium(II) acetate generates a furanocyclopropane which on standing rearranges to predominantly the *Z,E* isomer **127**. Using fairly standard reaction conditions, **127** is readily converted to **125**.



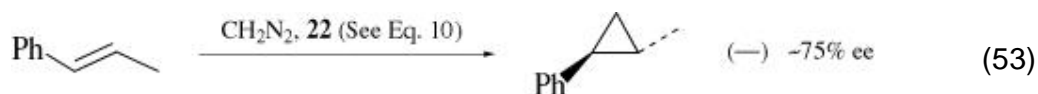
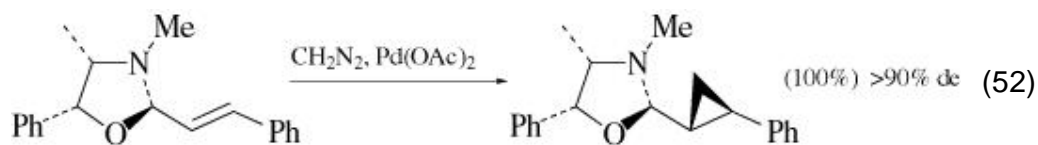
The reaction of pyrroles with carbenoids results in the formation of alkylation products unless the pyrrole nitrogen is *N*-acylated. (1, 179) This direct method for the preparation of pyrrole acetates has been used to prepare compounds of pharmaceutical interest such as **128** (180) and **129**. (216, 217)



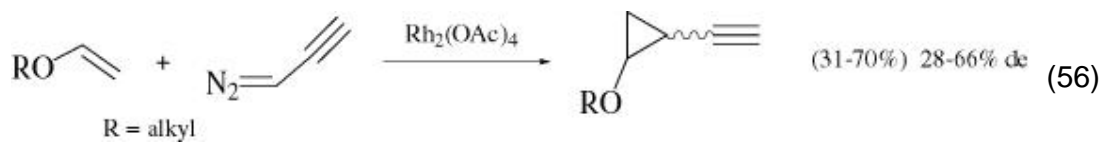
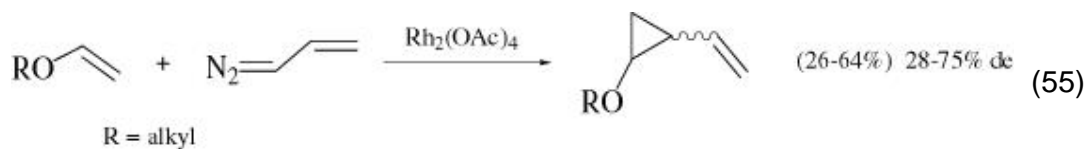
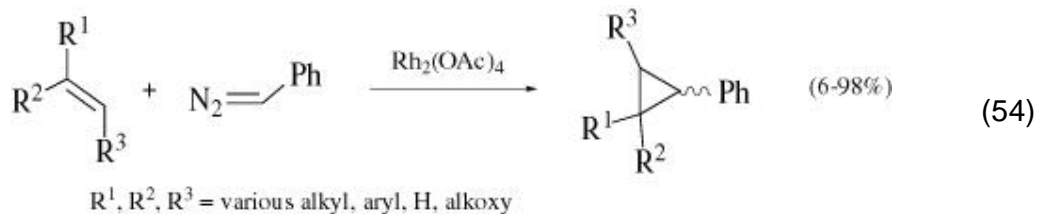
5. Comparison with Other Methods

Because of the vastness of the topic, the discussion of intermolecular carbenoid cyclopropanations has been limited to metal-catalyzed reactions of diazo compounds containing at least one electron-withdrawing group. Another source of carbenoids that has been used extensively are iodonium ylides. (218-222) It has been suggested that this carbenoid source is safer than diazo compounds, but overall it has not been demonstrated that they offer significant advantages over diazo compounds. (221, 222)

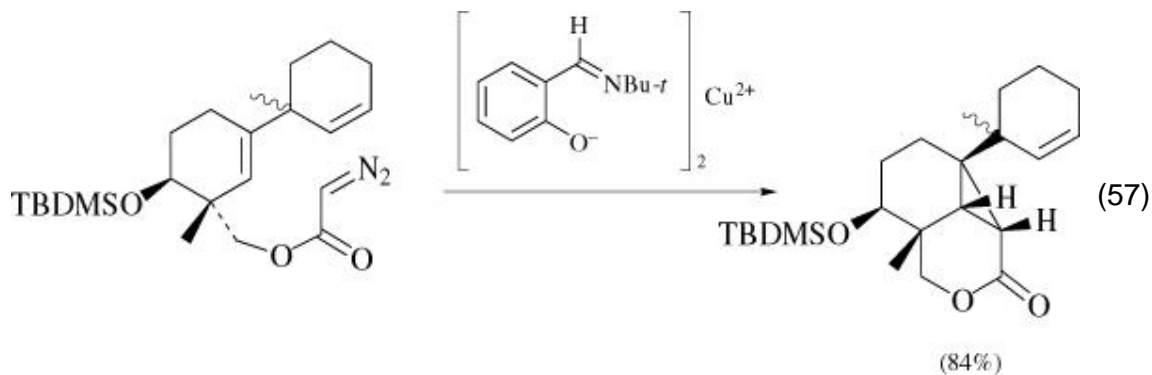
Metal-catalyzed decomposition of diazomethane in the presence of alkenes is a general synthetic process for the formation of cyclopropanes. (31) An alternative and more stable carbenoid precursor that can be used is silyldiazomethane. (223) Palladium acetate is the favored catalyst for these reactions (31) and it is likely that these reactions do not involve discrete metal carbenoid species. (37, 50) As cyclopropanation of alkenes containing electron-withdrawing groups is possible, (31) products similar to those from the reaction of diazoacetates and unpolarized alkenes can be formed. Chiral auxiliaries on the alkene have proved to be effective for asymmetric induction as illustrated in Eq. 52. (224, 225) The results for chiral catalysis, however, have tended to be disappointing, (226) but reasonable levels of asymmetric induction are obtained using the semicorrin copper complex **22** (Eq. 53). (123)

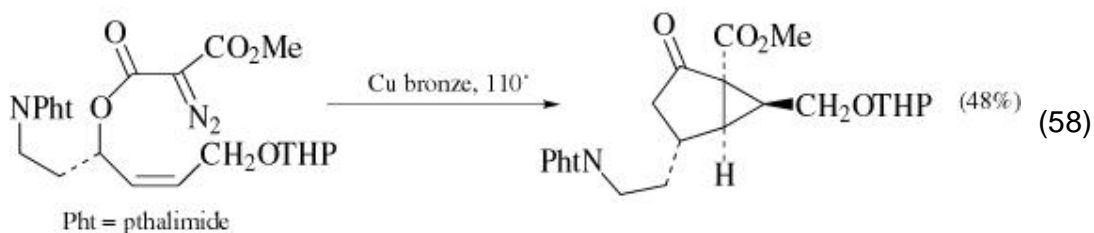


Other precursors to carbenoid species are phenyldiazomethanes, (32, 227) vinyldiazomethanes, (33, 228) and alkynyldiazomethanes. (33) Illustrative examples of cyclopropanations with these reagents are shown in Eqs. 54, 55, 56. These carbenoid precursors have not been extensively used in organic synthesis because they are unstable and difficult to handle.



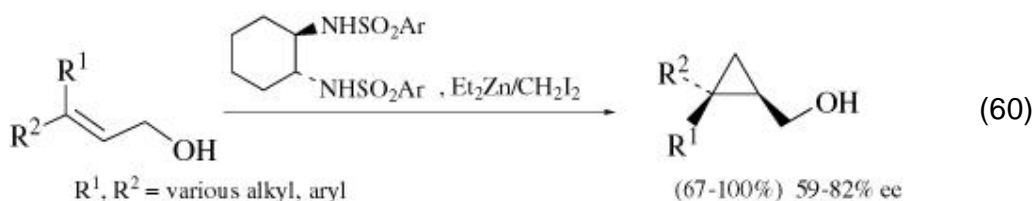
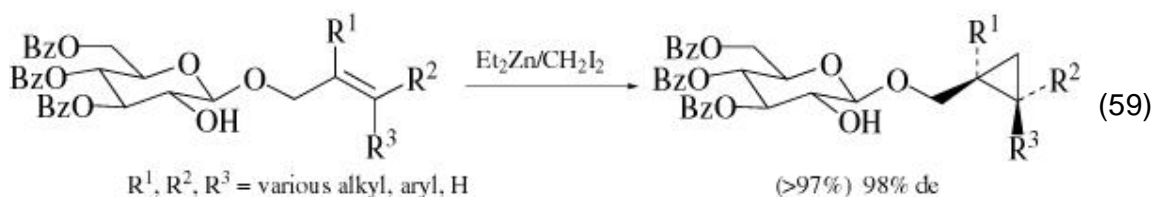
The use of carbenoid intermediates in intramolecular cyclopropanations is a very useful transformation because fused cyclopropanes are readily formed, and unlike the intermolecular version, full diastereocontrol is assured. (2, 12, 20, 229) Illustrative examples are shown in Eqs. 57 (230) and 58. (231)





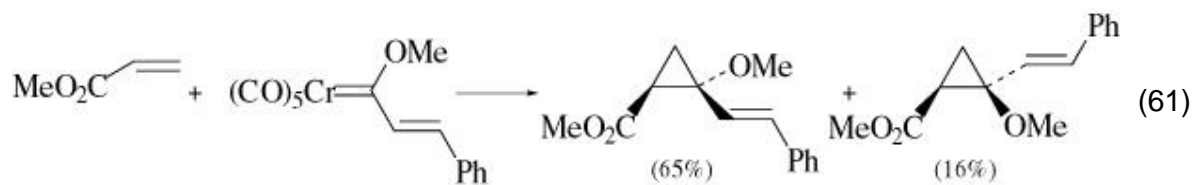
Further manipulation of the fused cyclopropanes has led to the synthesis of numerous natural products. (232) The asymmetric synthesis of fused cyclopropanes can be effectively achieved using a number of catalysts. The most effective to date appear to be the Doyle $\text{Rh}_2(\text{S-MEPY})_4$ catalyst **25** and related rhodium amide catalysts, (233-237) and the Evans C_2 -symmetric copper bisoxazoline catalyst **23**. (126, 238)

An alternative method for the cyclopropanation of alkenes is the Simmons-Smith reaction. (36) In this venerable reaction diiodomethane in the presence of zinc reagents is the carbenoid source. Improvements have been made by using samarium iodide instead of zinc reagents. (35) The asymmetric version of the reaction has now been achieved either by using chiral auxiliaries or chiral catalysis, as illustrated in Eq. 59 (239-242) and Eq. 60. (243, 244)



Although the Simmons-Smith reaction is a powerful reaction for methylene transfer to an alkene, unlike the metalcatalyzed decomposition of diazo compounds, is not applicable to a broad range of carbenoid functionality.

Cyclopropanes may also be formed from the reaction of alkenes with Fisher carbene complexes (245-249) (Eq. 61) and other stoichiometric organometallic sources of carbenes. (37)



Even though a range of diverse structures can be obtained using these organometallic complexes, the reactions are not particularly attractive because a stoichiometric quantity of the carbene complex is required.

A number of other methods are also available for the stereoselective synthesis of cyclopropanes. (24) Some of the most general are the following: 1,3-dipolar cycloaddition of diazoalkanes to various alkenes followed by extrusion of nitrogen; (250, 251) 1,4-addition of ylides to electron-deficient alkenes; (252) reaction of 1-phenylseleno-2-silylethenes with electron-deficient alkenes; (253-255) and palladium-catalyzed tandem alkylation and cyclization of stabilized anions to 1,4-dichloro-2-butene. (256)

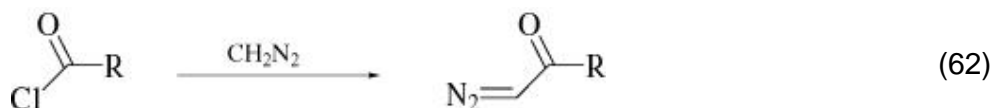
6. Experimental Considerations

6.1. Synthesis of Diazo Compounds

In order to be able to exploit metal-catalyzed cyclopropanation, practical methods are required for the synthesis of the diazo compounds. Excellent summaries of the methods available for the synthesis of diazo compounds have been published. (12, 22) Only a general overview is presented here. The most common methods for preparing diazo compounds containing at least one electron-withdrawing group are the following:

1. Reaction of activated carboxylic acid derivatives with diazoalkanes

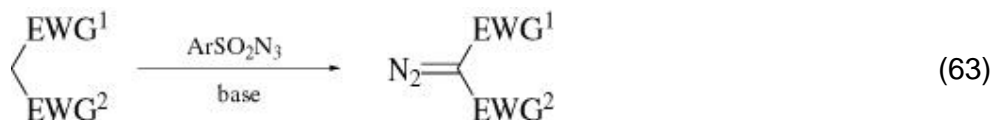
The reaction of diazomethane with acid chlorides or anhydrides is a well-established method for the synthesis of diazo ketones (Eq. 62). (257-260)



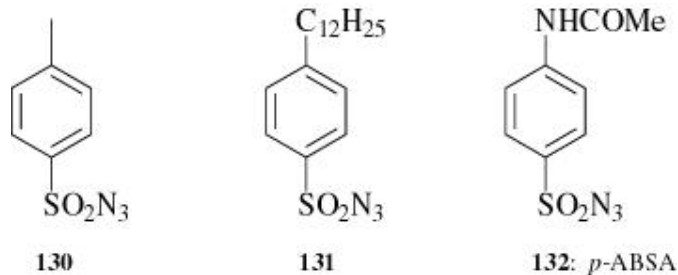
The reaction can be carried out with a very broad range of substrates and can be extended to functionalized diazoalkanes. (12) The major drawback with this synthetic method is the inherent danger of handling diazoalkanes. (259, 261) *Diazomethane needs to be handled extremely carefully because it is prone to explode even on contact with ground-glass joints.* (259, 261)

2. Diazo transfer reactions using arylsulfonyl azides

The diazo transfer reaction is a very practical method for the synthesis of diazo compounds (Eq. 63). (12, 22) A wide range of diazo transfer agents have been developed. (262)

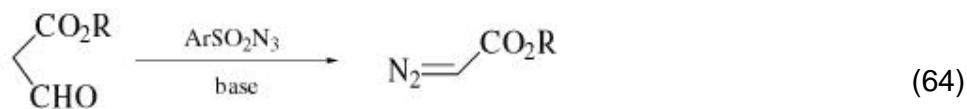


Traditionally, toluenesulfonyl azide (130) has been used as the diazo transfer agent, but owing to its potential explosive properties, (263, 264) safer reagents have been developed. A detailed overview of the safety issues regarding arylsulfonyl azides is available. (262) The two most practical reagents are *p*-dodecylbenzenesulfonyl azide (131) (265-267) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA, 132). (268, 269)



The first is ideally suited for the synthesis of crystalline diazo compounds because the sulfonamide byproduct is a highly soluble liquid that can be removed by trituration of the product. *p*-ABSAs is commercially available and is ideal for noncrystalline diazo compounds because the sulfonamide byproduct is highly crystalline and can be removed by trituration, leaving the diazo compound in solution. Various bases can be used in the reaction but the most commonly used are triethylamine and DBU. (12)

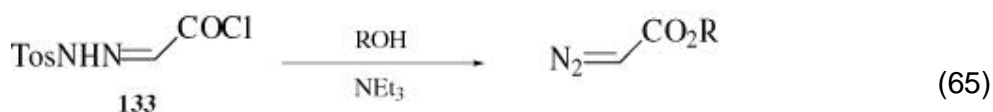
The diazo transfer reaction is ideally suited for the synthesis of compounds containing two electron-withdrawing groups, although phenyldiazoacetates and vinyldiazoacetates are readily formed from the diazo transfer reaction if DBU is used as base. (156, 268) Convenient methods have been developed for the preparation of diazo compounds with a single electron-withdrawing group, by following the diazo transfer reaction with deacylation (Eq. 64). (270) Acetyl, (78) benzoyl, (271, 272) and trifluoroacetyl (110, 273) groups have also been commonly used as the second electron-withdrawing group that would be lost in a deacylation step.



R = various alkyl, aryl

3. Thermolysis of tosylhydrazones

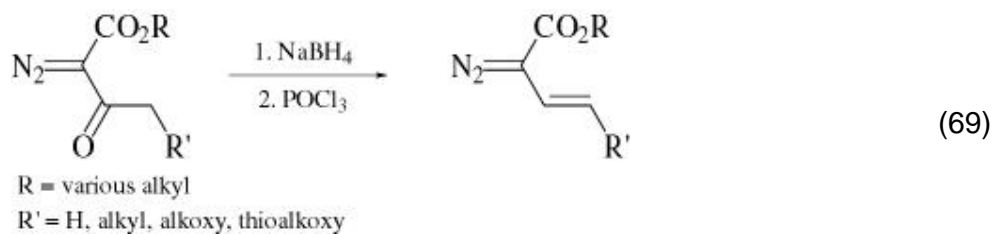
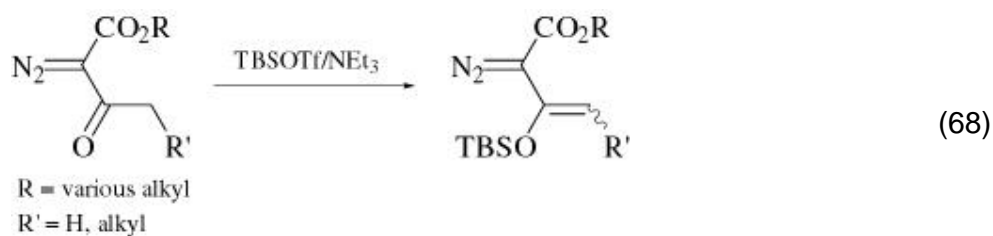
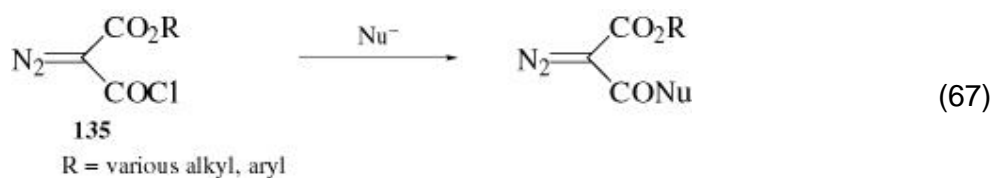
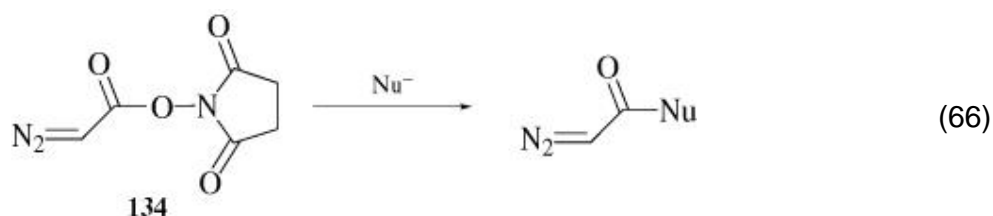
A well-established method for the synthesis of diazo compounds is the thermolysis of tosylhydrazones. (274) A particularly important application of this method is for the synthesis of alkyl diazoacetates by reaction of alcohols with tosylimido-glycolate 133 (Eq. 65). (275)



R = various alkyl, aryl

4. Functionalization of a diazocarbonyl derivative

In recent years it has become apparent that useful reactions can be carried out on diazo compounds without destruction of the diazo functionality. The chemistry of the succinamide **134**, which can be converted to a range of diazoacetate derivatives, is of notable practical application (Eq. 66). (233, 276) The diazomalonyl chloride **135** is another useful reagent for the synthesis of elaborate diazomalonate derivatives (Eq. 67). (277) Diazoacetoacetates may be silylated or reduced and then dehydrated to form vinyl diazoacetates (Eqs. 68 (144, 278) and 69). (279) The enolate of diazoacetate is also a useful reagent capable of undergoing aldol and alkylation reactions. (280)



A variety of miscellaneous methods are also available for the synthesis of diazo compounds containing at least one electron-withdrawing group. These include diazotization of amines, (281, 282) decomposition of tosylhydrazones, (283) and reaction of oximes with chloramine. (284)

7. Experimental Conditions

7.1. General Reaction Conditions

General reaction conditions for intermolecular carbenoid cyclopropanations are very practical. (75) Most of the catalysts are stable compounds or can be generated in situ from stable precursors. Rhodium(II) carboxylates are indefinitely stable in the open atmosphere. Copper(I) catalysts are generally formed in situ by reaction of the ligand with a copper salt such as copper(I) triflate. Many of the catalysts are introduced into the reaction as copper(II) complexes, but copper(II) is reduced to copper(I) under the reaction conditions, and it is most likely that copper(I) salts are the active catalysts in these reactions.

The diazo compound is usually added slowly to a stirred solution of the catalyst and the alkene. Usually, an excess of alkene is used in order to minimize side-reactions such as carbene dimerization, which can be very prevalent in the diazoacetate system. It has been shown, however, that good yields of cyclopropanes can be obtained with just one equivalent of alkene as long as syringe pump techniques are used for slow addition of the diazo compound. (94) Typically, the reaction is carried out under an inert atmosphere and anhydrous conditions. The standard solvent for many of the carbenoid reactions is dichloromethane but many other solvents, such as benzene, fluorobenzene, hexane, pentane, and diethyl ether have been used. It has become increasingly recognized that solvents can have a major effect on these reactions. Products derived from zwitterionic intermediates can be minimized by using nonpolar solvents. (63, 64, 185) Also, the enantioselectivity displayed by certain catalysts can be very solvent dependent. (58, 74)

7.2. Safety Considerations

Great care should be taken in handling diazo compounds because they are potentially toxic and can have explosive properties. Even though diazo compounds containing electron-withdrawing functionalities are much more stable than their diazoalkane counterparts, detailed studies on the potential dangers of many of the diazo compounds described in this review are not available. Therefore, diazo compounds should be handled carefully and all reactions should be carried out in a well-vented fume hood, behind a blast shield.

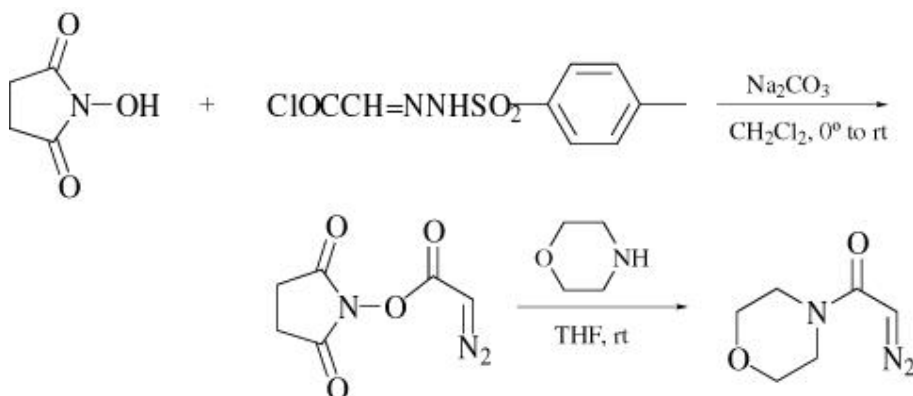
There have been reports in the literature of unpredicted explosions occurring when using toluenesulfonyl azide (263, 264) and methanesulfonyl azide. (263, 264) It is thus advisable that the more stable arylsulfonyl azides such as *p*-dodecylbenzenesulfonyl azide (265-267) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (268, 269) be used instead of toluenesulfonyl azide or

methanesulfonyl azide to carry out the diazo transfer reactions.

8. Experimental Procedures

8.1. General Procedures for the Preparation of Carbenoid Precursors

The following experiments are typically carried out behind a blast shield in a one- or three-necked flask equipped with a magnetic stirring bar (or a mechanical stirrer for large scale reactions) and either a dropping funnel or rubber septum. All reactions are performed under an inert atmosphere (nitrogen or argon). Addition of diazo compounds to the reaction mixture is accomplished via dropping funnel, cannula, or syringe pump.



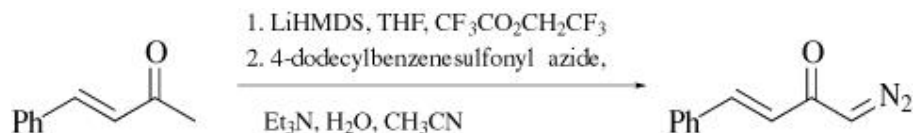
8.2. *N*-Diazoacetylmorpholine [Use of Succinimidyl Diazoacetate] (233, 276)

Glyoxylic acid chloride (*p*-toluenesulfonyl)hydrazone (285) (103.3 g, 0.500 mol) in CH₂Cl₂ (1.00 L) was added over 2 hours to a mechanically stirred suspension of *N*-hydroxysuccinimide (63.25 g, 0.550 mol) and Na₂CO₃ (79.5 g, 0.750 mol) in dry CH₂Cl₂ (0.75 L) maintained at 0°. The resulting mixture was stirred for an additional hour and then warmed to room temperature, where it was maintained for 3 hours, after which time it was filtered through a sand plug and then Celite[®]. The filtrate was concentrated under reduced pressure to provide crude succinimidyl diazoacetate as a brown-yellow solid.

Recrystallization from CH₂Cl₂/hexanes gave a light yellow crystalline product (43.0 g, 0.235 mol, 47% yield), (233) mp 113.5–115.0° (lit. (276) mp 119–120°); IR (CHCl₃) 2100 cm⁻¹; ¹H NMR (CDCl₃) 2.85 (s, 4 H), 5.13 (br s, 1 H); ¹³C NMR (CDCl₃) 25.4, 45.0, 162, 169.3; MS (*m/z*): 184 (*M* + 1, 21); Anal. Calcd. for C₆H₅N₃O₄: C, 39.03; H, 2.73; N, 22.95; O, 34.97. Found: C, 39.59; H, 2.8; N, 22.98; O, 35.1.

Morpholine (1.74 g, 20 mmol) in THF (5 mL) was treated with succinimidyl diazoacetate (1.83 g, 10 mmol) at room temperature for 1 hour. The solvent

was evaporated in vacuo, and the product was purified by chromatography on silica gel to give an amber yellow oil (1.51 g, 97%); IR (CHCl₃) 2100 cm⁻¹; ¹H NMR (CDCl₃) 3.39 (m, 4 H), 3.66 (m, 4 H), 4.98 (s, 1 H); ¹³C NMR (CDCl₃) 43.9, 66.4, 130.8, 164.89; MS (m/z): 155 (M⁺, 70).



8.2.1. (E)-1-Diazo-4-phenyl-3-buten-2-one [Detrifluoroacetylative Diazo Group Transfer Using 4-Dodecylbenzenesulfonyl Azide] (273)

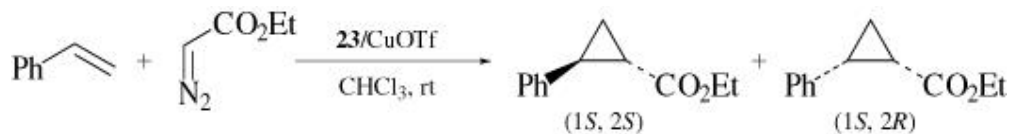
A 500-mL, three-necked, round-bottomed flask was equipped with a mechanical stirrer, nitrogen inlet adapter, and 150-mL pressure-equalizing dropping funnel fitted with a rubber septum. The flask was charged with dry THF (70 mL) and hexamethyldisilazane (15.9 mL, 0.075 mol), and then cooled in an ice-water bath while a 2.50 M solution of *n*-butyllithium (28.8 mL, 0.072 mol) in hexane was added dropwise over 5–10 minutes. After 10 minutes, the resulting solution was cooled to –78° in a dry ice-acetone bath, and a solution of *trans*-4-phenyl-3-buten-2-one (10.0 g, 0.068 mol) in dry THF (70 mL) was added dropwise over 25 minutes. The dropping funnel was washed with THF (2 × 5 mL) and then replaced with a rubber septum. The yellow reaction mixture was stirred for 30 minutes at –78°, and then 2,2,2-trifluoroethyl trifluoroacetate (10.1 mL, 0.075 mol) was added rapidly in one portion via syringe. After 10 minutes, the reaction mixture was poured into a 1-L separatory funnel containing diethyl ether (100 mL) and 5% aqueous HCl (200 mL). The aqueous layer was separated and extracted with diethyl ether (50 mL). The combined organic layers were washed with saturated NaCl solution (200 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure using a rotary evaporator to afford a yellow oil (18.61 g). This yellow oil was immediately dissolved in acetonitrile (70 mL) and transferred to a 500-mL, one-necked flask equipped with a magnetic stirring bar and a 150-mL pressure equalizing dropping funnel fitted with a nitrogen inlet adapter. Water (1.2 mL, 0.069 mol), triethylamine (14.3 mL, 0.103 mol), and a solution of 4-dodecylbenzenesulfonyl azide (267) (35.74 g, 0.103 mol) in acetonitrile (10 mL) were then added sequentially via the dropping funnel. The resulting yellow solution was stirred at room temperature for 6.5 hours and then poured into a 1-L separatory funnel containing diethyl ether (100 mL) and aqueous 5% NaOH (200 mL). The organic layer was separated, washed successively with 5% aqueous NaOH (3 × 200 mL), water (4 × 200 mL), and saturated NaCl (200 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated at reduced pressure to yield the crude reaction product as a light

brown oil (23.17 g). The crude reaction product was purified by column chromatography (silica gel, 5–10% diethyl ether/hexane) to furnish 9.80 g (83% yield) of (*E*)-1-diazo-4-phenyl-3-buten-2-one (mp 68–69°) as a bright yellow solid. IR (CCl₄) 3150–3000, 2090, 1645, 1600, 1445, 1360, 1180, 1140, 1095, 1070, 970, 690 cm⁻¹; ¹H NMR (CDCl₃) 5.54 (s, 1 H), 6.60 (d, *J* = 15.8 Hz, 1 H), 7.30–7.34 (m, 3 H), 7.46–7.49 (m, 2 H), 7.57 (d, *J* = 15.8 Hz, 1 H); ¹³C NMR (CDCl₃) 55.8, 123.5, 127.8, 128.5, 129.9, 134.0, 140.1, 184.0; Anal. Calcd for C₁₀H₈N₂O: C, 69.76; H, 4.68; N, 16.27. Found: C, 69.65; H, 4.84, N, 16.32.



8.2.2. Methyl (*E*)-2-Diazo-4-phenyl-3-buten-2-ate [Diazo Transfer Reaction with *p*-Acetamidobenzenesulfonyl Azide] (156)

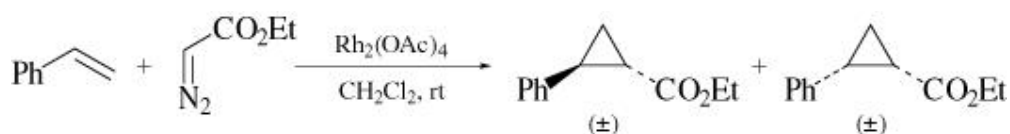
DBU (2.39 g, 15.7 mmol) was added to a stirred solution of methyl 4-phenylbutenoate (286) (2.05 g, 11.6 mmol) and *p*-acetamidobenzenesulfonyl azide (268, 269) (2.8 g, 11.8 mmol) in acetonitrile (75 mL) at 0°. After the mixture was stirred for 4 hours, saturated aqueous NH₄Cl solution was added, and the mixture was extracted twice with CH₂Cl₂. The organic layer was then dried (MgSO₄), and the solvent was evaporated under reduced pressure. The residue was triturated with ether/pentane (50:50), filtered, and the solvent was evaporated under reduced pressure. Further purification of the product by chromatography on silica gel with ether/petroleum ether (1:4) as the eluent gave methyl (*E*)-2-diazo-4-phenyl-3-buten-2-ate (2.08 g, 89% yield) as a red solid; IR (neat) 3010, 2940, 2040, 1695, 1620, 1590, 1440 cm⁻¹; ¹H NMR (CDCl₃) 3.81 (s, 3 H), 6.15 (d, *J* = 16.2 Hz, 1 H), 6.44 (d, *J* = 16.2 Hz, 1 H), 7.34–7.15 (m, 5 H).



8.3. General Procedures for Carbenoid Cyclopropanation Reactions

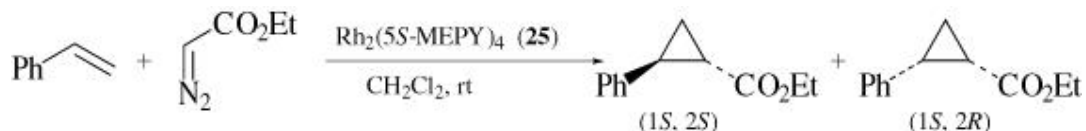
8.3.1. Ethyl (1*S*,2*S*)-2-Phenylcyclopropanecarboxylate and Ethyl (1*S*,2*R*)-2-Phenylcyclopropanecarboxylate [Asymmetric Cyclopropanation of Styrene with Ethyl Diazoacetate in the Presence of Copper Bisoxazoline Catalyst 23] (126)

To a suspension of CuOTf (0.0068 g, 0.027 mmol) was added a solution of **23** (8.1 mg, 0.028 mmol) in CHCl₃ (9 mL). After 1 hour, the mixture was passed through a filter cannula comprised of a needle with the hub packed with glass wool. To this was added styrene (1.6 mL, 14 mmol), and then a solution of ethyl diazoacetate (0.285 mL, 2.71 mmol) in CHCl₃ (10 mL) was added dropwise over 1.5 hours. After 14 hours, the mixture was concentrated in vacuo to a green oil. This was purified by flash chromatography (3 × 30 cm silica, 10:90 EtOAc/hexane as eluent). The products were isolated as a clear oil (0.399 g, 77%, trans:cis = 73:27). The isomers obtained were separated by medium pressure liquid chromatography (Michel-Miller column, 3:97–10:90 EtOAc/hexane as eluent) and identified. Ethyl (1*S*,2*S*)-2-phenylcyclopropanecarboxylate: mp 37.7–39.1°; IR (CCl₄) 3090, 3070, 3040, 2990, 2910, 2880, 1730, 1610, 1500, 1480, 1460, 1440, 1410, 1390, 1370, 1340, 1325, 1305, 1290, 1265, 1220, 1180, 1120, 1100, 1080, 1045, 1020, 950, 935, 850 cm⁻¹; ¹H NMR (CDCl₃) 7.1–7.4 (m, 5 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 2.52 (ddd, *J* = 4.1, 6.4, 9.2 Hz, 1 H), 1.90 (ddd, *J* = 4.2, 5.3, 8.4 Hz, 1 H), 1.60 (m, *J* = 4.4, 5.1, 9.4 Hz, 1 H), 1.31 (ddd, *J* = 4.6, 6.5, 8.4 Hz, 1 H), 1.28 (t, *J* = 7.1 Hz, 3 H); [α]_D + 296° (c 0.88, CHCl₃); 99% ee. Ethyl (1*S*,2*R*)-2-phenylcyclopropanecarboxylate: IR (thin film) 3090, 3060, 3030, 2980, 2940, 2910, 2880, 1730, 1605, 1495, 1480, 1450, 1440, 1400, 1380, 1355, 1270, 1220, 1180, 1155, 1095, 1080, 1030, 955, 865, 850, 790, 750, 720, 695 cm⁻¹; ¹H NMR (CDCl₃) 7.1–7.3 (m, 5 H), 3.87 (q, *J* = 7.1 Hz, 2 H), 2.58 (m, 1 H), 2.08 (ddd, *J* = 5.6, 7.8, 9.3 Hz, 1 H), 1.71 (m, *J* = 5.3, 7.5 Hz, 1 H), 1.34 (ddd, *J* = 5.1, 7.9, 8.6 Hz, 1 H), 0.97 (t, *J* = 7.1 Hz, 3 H); [α]_D + 18.6° (c 1.01, CHCl₃); 97% ee.



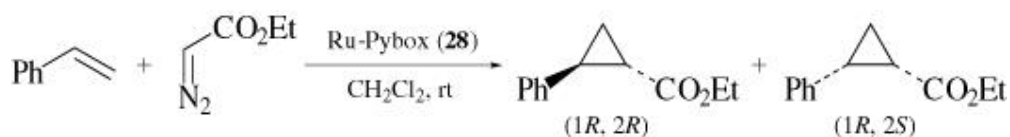
8.3.2. Ethyl 2-Phenylcyclopropanecarboxylate [Reaction of Ethyl Diazoacetate with Styrene in the Presence of Rh₂(OAc)₄] (78)

Ethyl diazoacetate (57 mg, 0.50 mmol) dissolved in anhydrous CH₂Cl₂ (3.0 mL) was added at a controlled rate over a 5-hour period to a stirred mixture of styrene (520 mg, 5.0 mmol) and Rh₂(OAc)₄ (2.2 mg, 0.005 mmol) in CH₂Cl₂ (3.0 mL) at room temperature. Two hours after addition was complete the reaction solution was passed through a short alumina column with CH₂Cl₂ as the eluent to remove the catalyst. Solvent and excess styrene were distilled under reduced pressure to give ethyl *trans*- and *cis*-2-phenylcyclopropanecarboxylate (88 mg, 93%, 62:38).



8.3.3. Ethyl (1S,2S)-2-Phenylcyclopropanecarboxylate and Ethyl (1S,2R)-2-Phenylcyclopropanecarboxylate [Asymmetric Cyclopropanation of Styrene with Ethyl Diazoacetate in the Presence of $\text{Rh}_2(5\text{S-MEPY})_4$ (25)] (108, 287)

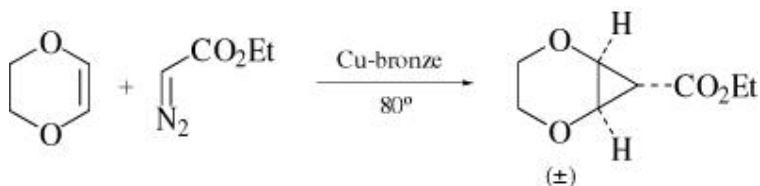
To a light blue solution of styrene (1.04 g, 10.0 mmol) and $\text{Rh}_2(5\text{S-MEPY})_4$ (25) (7.7 mg, 0.010 mmol) in anhydrous CH_2Cl_2 (20 mL) under N_2 was added ethyl diazoacetate (0.114 g, 1.00 mmol) in CH_2Cl_2 (10 mL) through a syringe pump at a rate of 0.5 mL/hour. After addition was complete, the mixture was filtered through a 1-cm plug of silica gel to separate the catalyst, and the plug was eluted with CH_2Cl_2 (30 mL). The excess styrene was removed and the residue was purified by bulb-to-bulb distillation at 60–80°/0.05 Torr to give the products as a clear oil (0.112 g, 59%). GC analysis was performed prior to and following distillation without noticeable change in isomer ratios trans:cis = 56:44). Diastereomer ratios were obtained using a capillary methyl silicone column, and enantiomer separation was performed by GC, using a Chiraldex- γ -cyclodextrin-TFA column (58% ee trans, 33% ee cis).



8.3.4. Ethyl (1R,2R)-2-Phenylcyclopropanecarboxylate and Ethyl (1R,2S)-2-Phenylcyclopropanecarboxylate [Asymmetric Cyclopropanation of Styrene with Ethyl Diazoacetate in the Presence of $\text{trans-RuCl}_2(\text{Pybox-}ip)(\text{ethylene})$ (28)] (106)

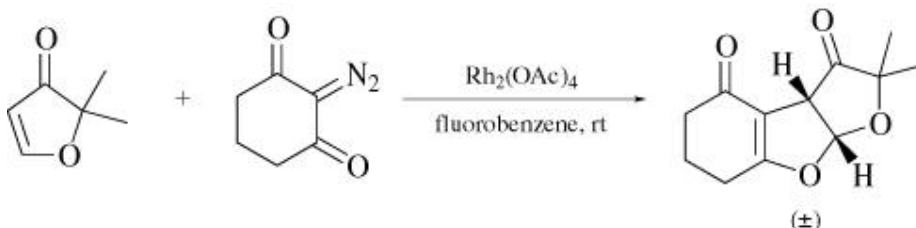
To a solution of $\text{trans-RuCl}_2(\text{Pybox-}ip)(\text{ethylene})$ (28) (30 mg, 0.06 mmol) and styrene (1.7 mL, 15 mmol) in CH_2Cl_2 (2.0 mL) was added a dichloromethane solution of ethyl diazoacetate (3.0 mmol, ~1 M) through a microsyringe controlled by a mechanical feeder ~4 $\mu\text{L}/\text{drop}$, ~0.4 mL/hour) for 8 hours at 20–25° under an argon atmosphere. After stirring for an additional 10 hours, the reaction mixture was concentrated under reduced pressure. The residual oil was subjected to silica gel column chromatography with hexane-ether as eluent to give an oily mixture (416 mg, 73% yield) of methyl *trans*-2-phenylcyclopropane-1-carboxylate and methyl

cis-2-phenylcyclopropane-1-carboxylate *trans*:*cis* = 91:9). Enantiomeric purity was measured by GLPC (Astec, Chiraldex B-DA, 30 m × 0.25 mm) (89% ee *trans*, 79% ee *cis*).



8.3.5. Ethyl 2,5-Dioxabicyclo[4.1.0]heptanecarboxylate [Reaction of Ethyl Diazoacetate with *p*-Dioxene in the Presence of Copper-bronze] (95)

Ethyl diazoacetate (2.85 g, 25 mmol) was added dropwise to a stirred suspension of copper-bronze (300 mg) in *p*-dioxene (4.5 g, 50 mmol), kept at 80° under nitrogen, and thereafter the stirring and heating was continued for 0.5 hour. After removal of the excess *p*-dioxene by vacuum distillation the mixture was filtered through Celite. The catalyst was washed with ether and the combined filtrates were evaporated. Distillation of the residue yielded 3.45 g (80% yield) of a colorless liquid, ethyl 2,5-dioxabicyclo[4.1.0]heptanecarboxylate: bp 57–59° (0.1 Torr); IR (C = O) 1718 cm⁻¹; ¹H NMR 1.20 (t, *J* = 7 Hz, Me, 3 H), 2.12 (t, *J* = 3 Hz, COCH, 1 H), 3.63 (s, 4 H, 2 OCH₂), 3.89 (d, *J* = 3 Hz, 2 OCH, 2 H), 4.07 (q, *J* = 7 Hz, OCH₂ of OEt, 2 H); ¹³C NMR 13.9 (Me), 24.4 (C-7), 56.8 (C-1, C-6), 60.0 (OCH₂), 62.5 (C-3, C-4), 170.2 (C = O).

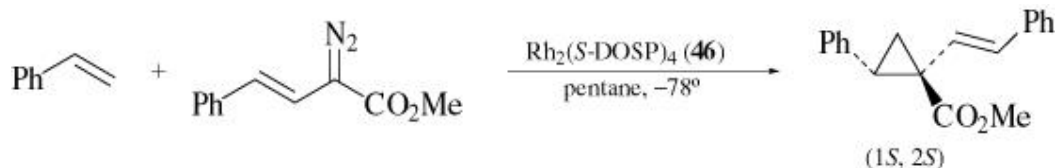


8.3.6. (3aS*,

8aR*)-2,2-Dimethyl-2,3,3a,6,7,8a-hexahydro-5H-1,8-dioxacyclopent[a]indene-3,4-dione [Reaction of 2-diazo-1,3-cyclohexanedione with 2,2-Dimethyl-3(2H)-furanone in the Presence of Rh₂(OAc)₄] (136)

To a solution of Rh₂(OAc)₄ (0.192 g, 0.43 mmol) and 2,2-dimethyl-3(2H)-furanone (4.871 g, 43.44 mmol) in fluorobenzene (50 mL) was added a solution of 2-diazo-1,3-cyclohexanedione (3.0 g, 21.7 mmol) in fluorobenzene (4 mL) at room temperature. The reaction mixture was stirred

for 10 hours. Evaporation and filtration through Celite with 25% ethyl acetate in hexane afforded a viscous oil which upon treatment with 20% ether in hexane gave 2.703 g (56%) of a gummy solid: ^1H NMR (300 MHz, CDCl_3), δ 6.52 (d, $J = 6.6$ Hz, 1 H), 3.95 (d, $J = 6.6$ Hz, 1 H), 2.54–2.01 (m, 6 H), 1.32 (s, 6 H); IR (KBr) 2956, 1740, 1628, 1397, 1330, 1186, 1132, 1100, 915 cm^{-1} ; EIMS (m/z , rel. intensity): 222, (M^+ , 100), 204 (14), 179 (22), 176 (13), 152 (11), 136 (10), 124 (4), 108 (4); HRMS m/z (M^+) for $\text{C}_{12}\text{H}_{14}\text{O}_4$ calcd 222.0892, found 222.0894.



8.3.7. (1S,2S)-Methyl 2 β -Phenyl-1 β -[2-(Z)-styryl]cyclopropane-1 α -carboxylate [Asymmetric Cyclopropanation of Styrene with Methyl (E)-2-Diazo-4-phenyl-3-butenolate in the Presence of $\text{Rh}_2(\text{S-DOSP})_4$ (46)] (58)

A mixture of styrene (44.2 g, 424 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (46) (1.58 g, 0.85 mmol) in pentane (350 mL) was stirred at -78° under an argon atmosphere. To this solution was added methyl (E)-2-diazo-4-phenyl-3-butenolate (17.2 g, 84.8 mmol) in pentane (0.12 M) over 30 minutes, and the reaction mixture was then stirred at -78° for 24 hours. The mixture was then concentrated in vacuo, and the residue was purified on silica using ether/petroleum ether (0:100 to 10:90) as the eluent to give (1S,2S)-methyl 2 β -phenyl-1 β -[2-(Z)-styryl]cyclopropane-1 α -carboxylate (16.05 g, 68%) as a white solid (mp $57\text{--}60^\circ$; 98% ee); IR (CHCl_3) 3110, 3090, 3060, 2980, 2950, 2880, 1735 cm^{-1} ; ^1H NMR (148) (CDCl_3) 1.85 (dd, $J = 7.3$, 5.1 Hz, 1 H), 2.05 (dd, $J = 9.1$, 5.1 Hz, 1 H), 3.04 (dd, $J = 9.1$, 7.3 Hz, 1 H), 3.77 (s, 3 H), 6.15 (d, $J = 15.9$, 1 H), 6.37, (d, $J = 15.9$ Hz, 1 H), 7.12–7.28 (m, 10 H); ^{13}C NMR (CDCl_3) 18.5, 33.2, 34.9, 52.3, 124.0, 126.1, 126.7, 127.2, 127.9, 128.3, 129.0, 133.0, 135.4, 137.0, 174.1; $[\alpha]_D^{25} - 166^\circ$ (c 1.1, CHCl_3); Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_2$: C, 81.99; H, 6.52. Found: C, 81.74; H, 6.53.

9. Tabular Survey

Tables I–III cover achiral cyclopropanations of alkenes. They are divided according to the three major types of carbenoid systems: those with a single electron-withdrawing group, those with two electron-withdrawing groups, and those with both an electron-withdrawing and an electron-donating group. Charts appearing before the Tables section are used to show structures of more complicated catalysts and assign them numbers for use in the Tables section. Chart 1 depicts non-chiral catalysts.

Tables IV–VII cover the asymmetric cyclopropanation of alkenes. The three major types of carbenoids are described together in these tables. In Table IV the use of chiral auxiliaries is described, while in Tables V–VII, the use of chiral catalysis is described. Because of the vast range of chiral catalysts that have been used for asymmetric cyclopropanation, Tables V–VII are divided according to the metal used, copper, rhodium, and miscellaneous metals. Charts 2–5 depict chiral catalysts.

Tables VII–X cover both achiral and asymmetric reactions of carbenoids with dienes, furans and pyrroles. The three major types of carbenoids are described together in these tables.

Entries in the Tables are ordered by increasing carbon count (boldface type) of the carbenoid precursor. Where the carbenoid precursor structure contains one or more “R” groups, the carbon count for the precursor with the substituents defined is also given (plain type). For a particular carbon count of carbenoid precursor, the alkene substrates are also ordered by increasing carbon count, followed by increasing hydrogen count. Protecting groups are omitted from the carbon count. Unspecified yields are indicated by (—), while missing or unspecified trans/cis ratios, enantiomeric excesses, and absolute stereochemistries are indicated by —. The term “ee” is used to describe the asymmetric induction of the cyclopropanation. In order to avoid confusion with the formation of cis and trans cyclopropane isomers, the term “ee” is used even when chiral auxiliaries exist on the carbenoid and the resulting cyclopropanes, prior to removal of the auxiliary, are actually diastereomers.

Note that some “R” groups, especially in Table IV, are designated by the compound from which the ester in the carbenoid precursor is derived, such as pantolactone and methyl lactate. This convention allows a clearer representation of the precursor than the alternative chemical name.

The tables contain all examples that could be found in the literature from 1970 through June 1999.

Chart 1. Non-Chiral Catalyst Complexes

[View PDF](#)

Chart 2. Chiral Copper C₂-Symmetric Catalyst Complexes

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Chart 3. Chiral Copper Non-C₂-Symmetric Catalyst Complexes

[View PDF](#)

Chart 4. Chiral Rhodium Catalysts

[View PDF](#)

Chart 5. Other Chiral Metal Catalysts

[View PDF](#)

Table I. Diastereoselective Cyclopropanation of Alkenes Using Diazoacetates and Related Systems

[View PDF](#)

Table II. Diastereoselective Cyclopropanation of Alkenes Using Diazoacetoacetates, Diazomalonates, and Related Systems

[View PDF](#)

Table III. Diastereoselective Cyclopropanation of Alkenes Using Vinyl and Phenyl Diazoacetates

[View PDF](#)

Table IV. Asymmetric Cyclopropanation of Alkenes Using Chiral Auxiliaries

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Table V. Asymmetric Cyclopropanation of Alkenes Using Chiral Copper Catalysts

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Table VI. Asymmetric Cyclopropanation of Alkenes Using Chiral Rhodium Catalysts

[View PDF](#)

Table VII. Asymmetric Cyclopropanation of Alkenes Using Miscellaneous Chiral Catalysts

[View PDF](#)

Table VIII. Reaction of Carbenoids with Dienes

[View PDF](#)

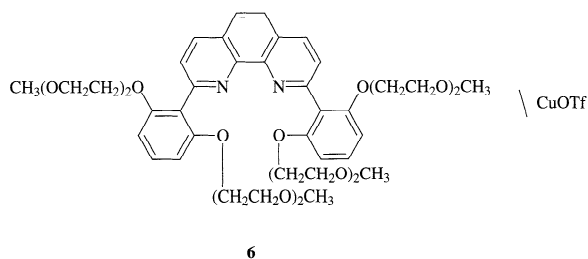
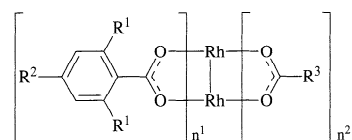
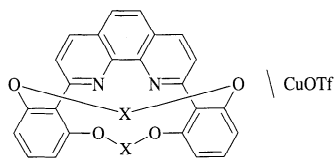
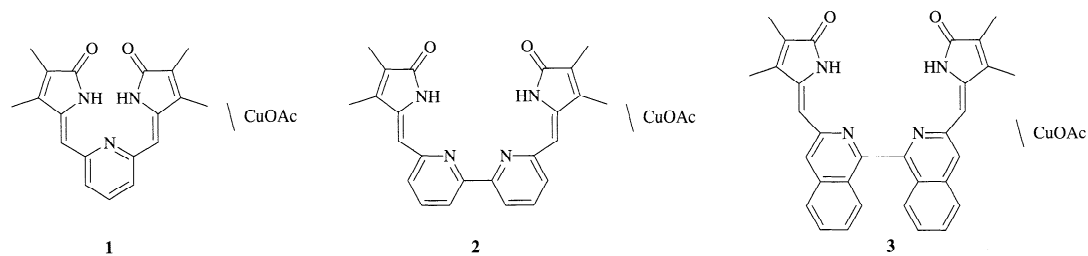
Table IX. Reaction of Carbenoids with Furans

[View PDF](#)

Table X. Reaction of Carbenoids with Pyrroles

[View PDF](#)

CHART 1. NON-CHIRAL CATALYST COMPLEXES



	R ¹	R ²	R ³	n ¹	n ²
7a:	Ph	Ph	Me	3	1
7b:	Ph	Ph	Me	4	0
7c:	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Me	3	1
7d:	4-MeC ₆ H ₄	4-MeC ₆ H ₄	Me	4	0
7e:	4-biphenyl	Ph	Me	3	1
7f:	4-biphenyl	Ph	Me	4	0
7g:	4- <i>t</i> -BuC ₆ H ₄	Ph	Me	2	2
7h:	4- <i>t</i> -BuC ₆ H ₄	Ph	Me	3	1
7i:	4-MeC ₆ H ₄	4-MeC ₆ H ₄	<i>t</i> -Bu	3	1
7j:	4-MeC ₆ H ₄	4-MeC ₆ H ₄	CF ₃	3	1

CHART 1. NON-CHIRAL CATALYST COMPLEXES (Continued)

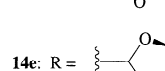
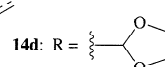
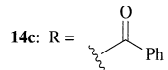
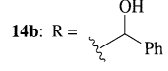
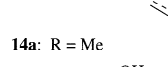
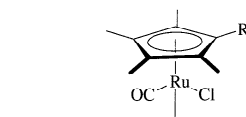
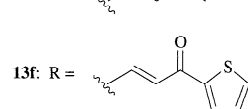
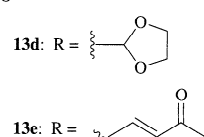
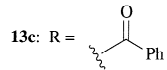
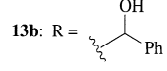
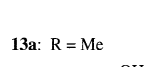
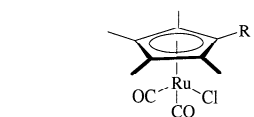
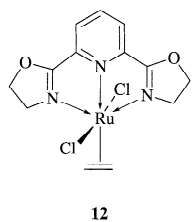
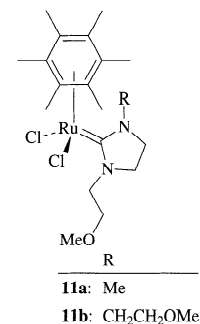
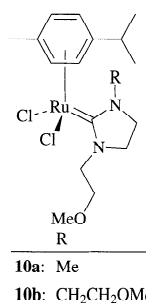
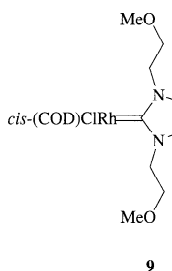
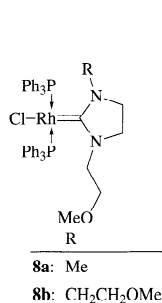
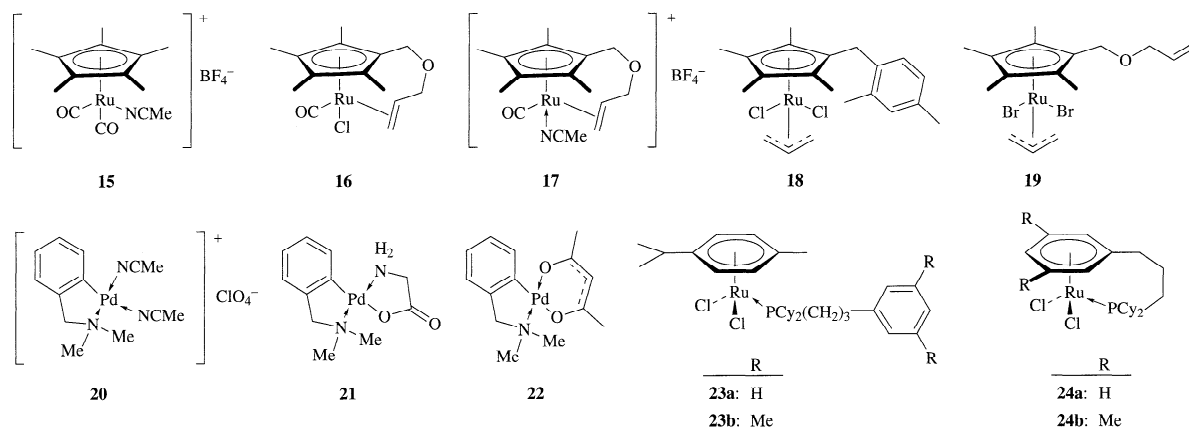
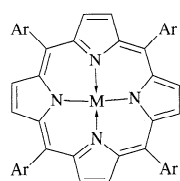


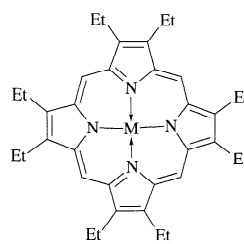
CHART 1. NON-CHIRAL CATALYST COMPLEXES (Continued)



46



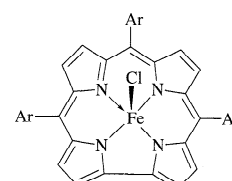
Ar	M
25a:	4-MeC ₆ H ₄ Ru, TTP
25b:	4-MeC ₆ H ₄ Os, TTP
25c:	4-MeC ₆ H ₄ Rh, TTP
25d:	mesityl Ru, TMP
25e:	mesityl Os, TMP
25f:	mesityl Rh, TMP
25g:	C ₆ F ₅ Fe, TpFPP



M

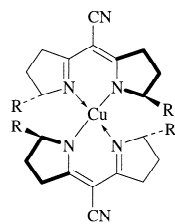
26a: Ru, OEP

26b: Os, OEP

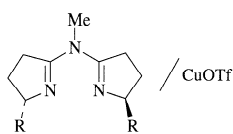


27: Ar = C₆F₅

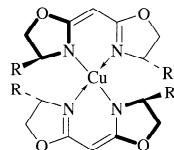
CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES



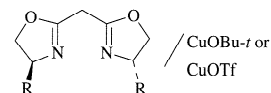
R
28a: CMe₂OH
28b: CH₂OTBDMS
28c: CO₂Me



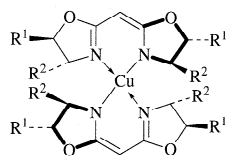
R
29a: CMe₂OTMS
29b: CH₂OTBDMS
29c: CMe₂OTBDMS



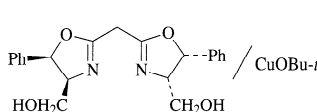
R
30a: *i*-Pr
30b: *t*-Bu
30c: Ph
30d: Bn
30e: C(OH)Me₂



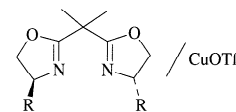
R
31a: *i*-Pr
31b: *t*-Bu
31c: Ph
31d: Bn
31e: C(OH)Me₂
31f: (*S*)-CHEt(Me)



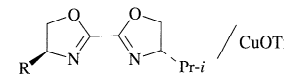
R ¹	R ²
32a: Ph	Me
32b: H	CH ₂ OH
32c: H	Fr
32d: Ph	CH ₂ OTBDMS
32e: 4-O ₂ NC ₆ H ₄	CH ₂ COPh
32f: 4-O ₂ NC ₆ H ₄	CH ₂ OH



33

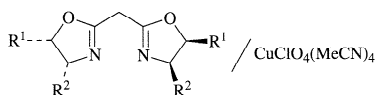


R
34a: *i*-Pr
34b: *t*-Bu
34c: Ph / CuCl₂
34d: Bn / CuCl₂

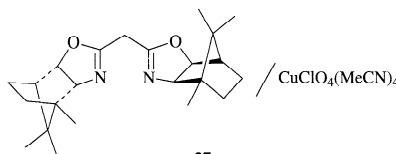


35

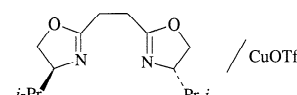
CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



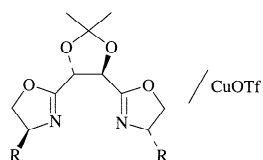
R ¹	R ²
36a: Ph	Ph
36b: Ph	Me
36c: <i>t</i> -Bu	Et



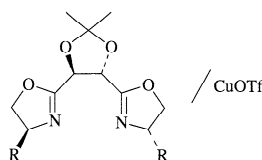
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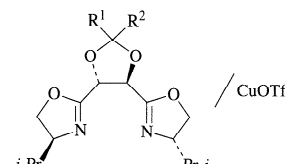
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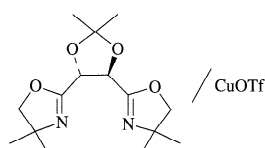
R
39a: *i*-Pr
39b: *t*-Bu
39c: Ph
39d: Bn
39e: *i*-Bu



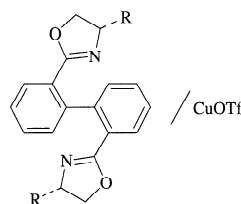
R
40a: *i*-Pr
40b: *t*-Bu
40c: Ph
40d: Bn



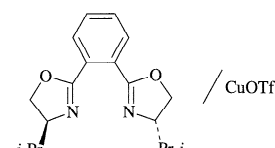
R ¹	R ²
41a: H	H
41b: Et	Et
41c: <i>n</i> -Bu	<i>n</i> -Bu
41d: Me	H
41e: Me	Ph
41f: Ph	H



42

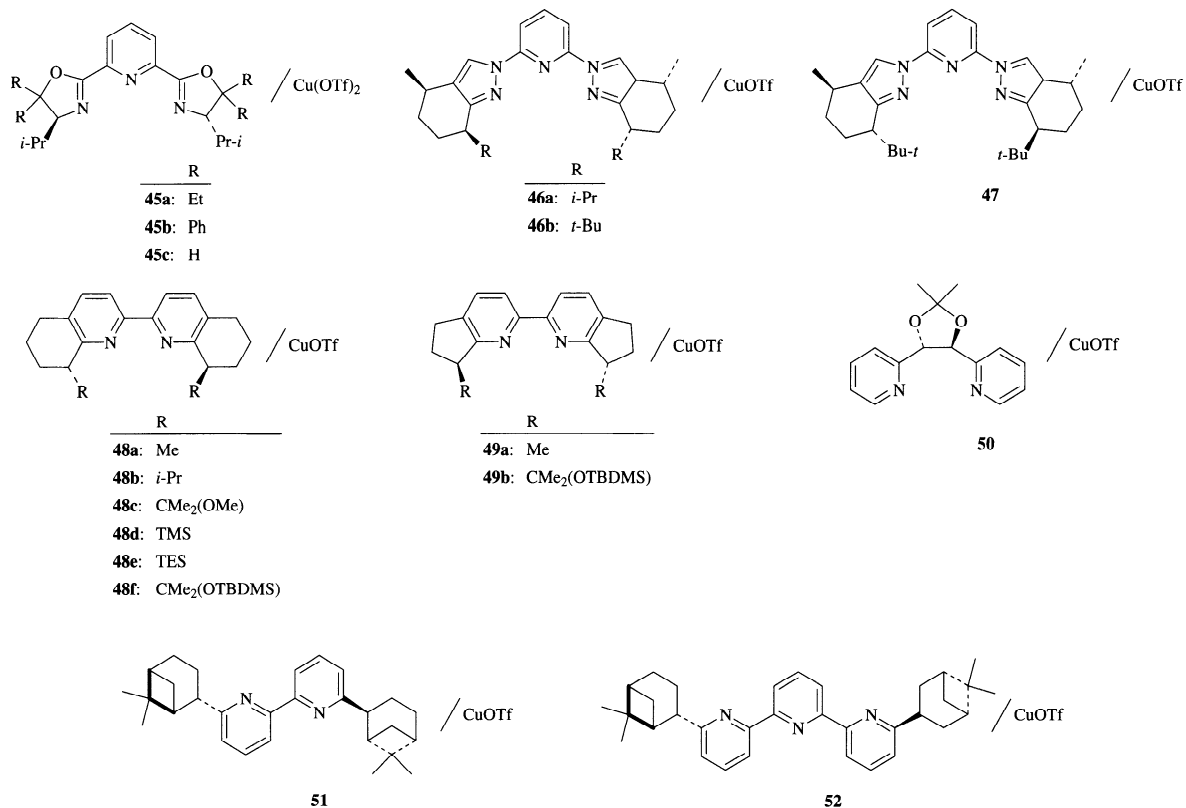


R
43a: *i*-Pr
43b: *t*-Bu



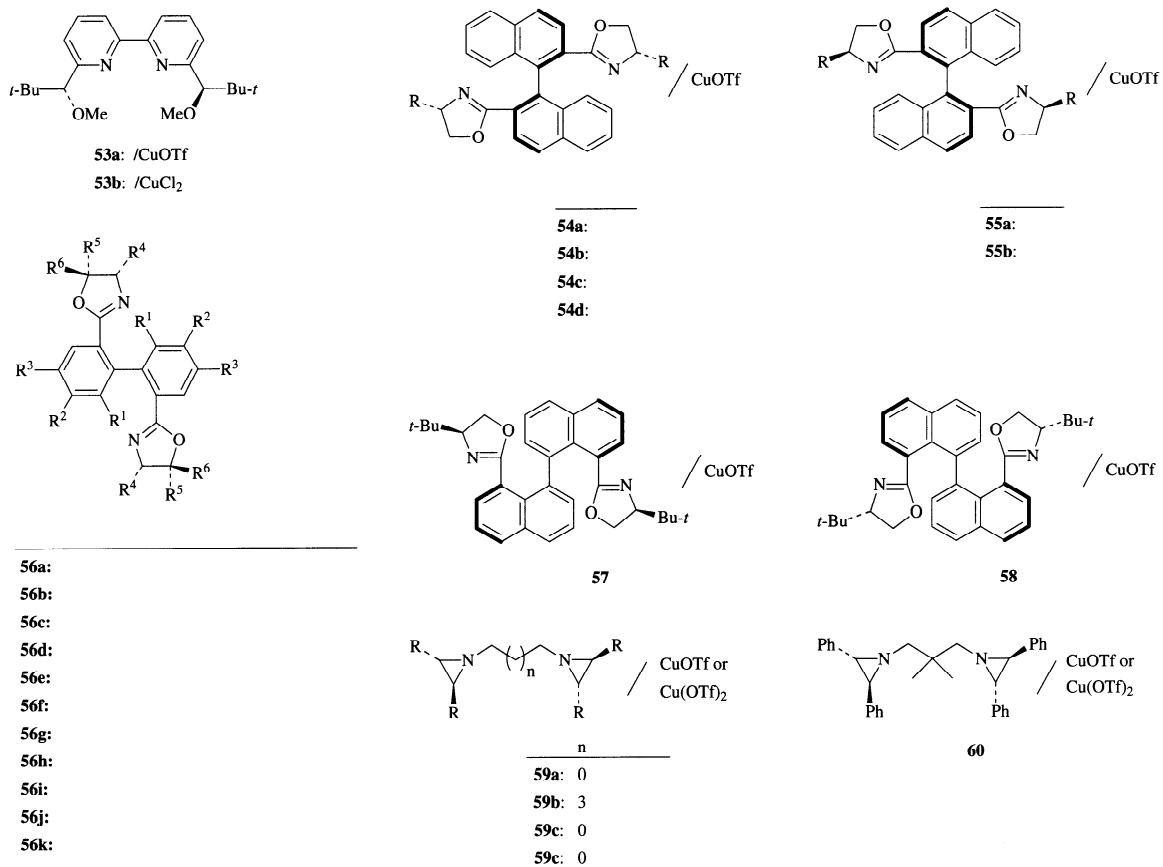
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CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



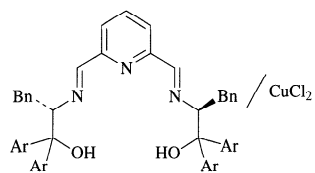
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CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES (Continued)

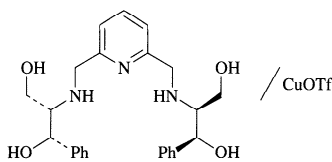


50

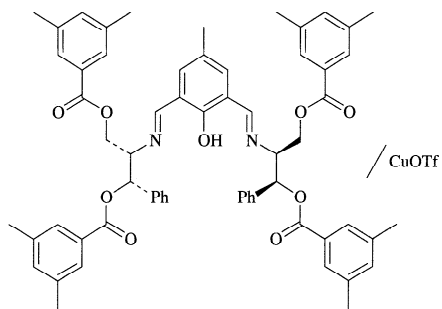
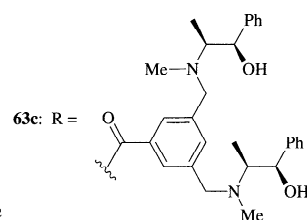
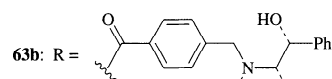
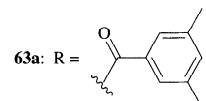
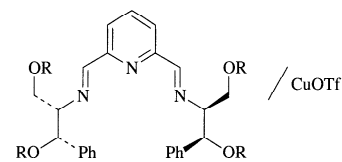
CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



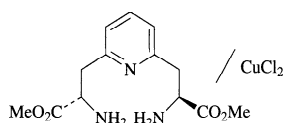
61: Ar = 2-MeOC₆H₄



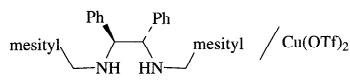
62



64

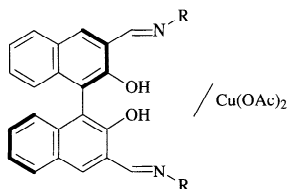


65

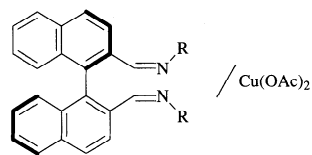


66

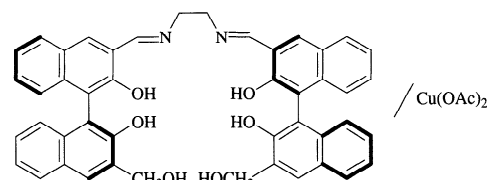
CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



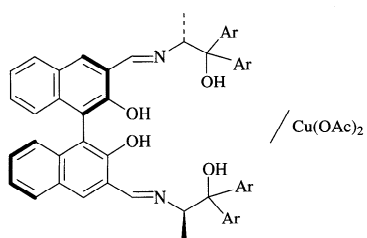
- R
- 67a: *i*-Pr
 - 67b: (*S*)-CHPh(Me)
 - 67c: (*R*)-CHPh(Me)
 - 67d: Ph
 - 67e: (*R*)-CH(CH₂OH)(Et)
 - 67f: (*S*)-CH(CH₂OH)(Et)
 - 67g: D-norephedrinyl
 - 67h: L-norephedrinyl
 - 67i: (*S*)-CH(CPh₂OH)(Pr-*i*)



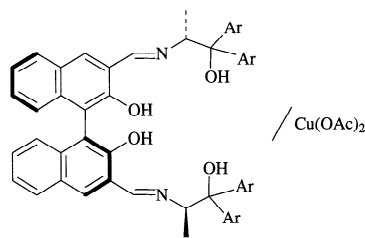
- R
- 68a: D-norephedrin
 - 68b: L-norephedrin



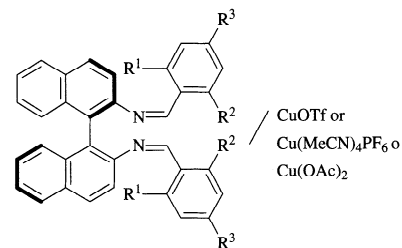
69



70: Ar = 2-(*n*-C₈H₁₇O)-5-*t*-BuC₆H₃

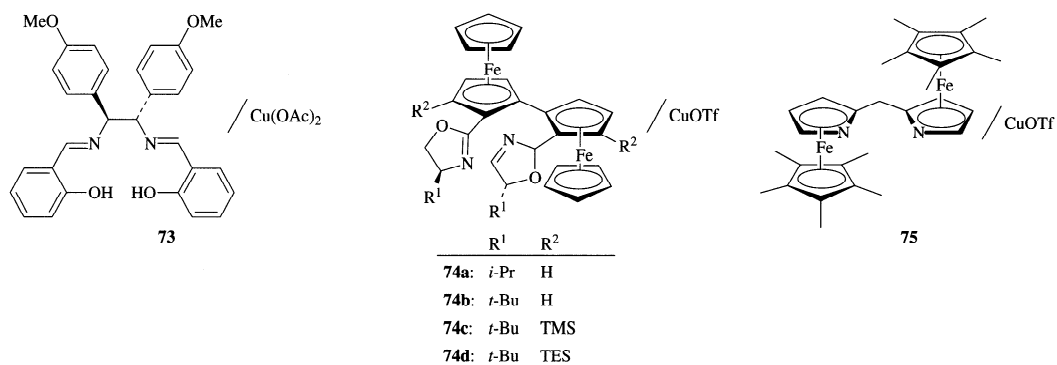


71: Ar = 2-(*n*-C₈H₁₇O)-5-*t*-BuC₆H₃



- | | R ¹ | R ² | R ³ |
|------|----------------|----------------|----------------|
| 72a: | Cl | Cl | H |
| 72b: | Me | Me | H |
| 72c: | Cl | Cl | Cl |
| 72d: | Br | Br | Br |
| 72e: | Me | Me | Me |
| 72f: | <i>i</i> -Pr | <i>i</i> -Pr | <i>i</i> -Pr |
| 72g: | OH | H | H |

CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



53

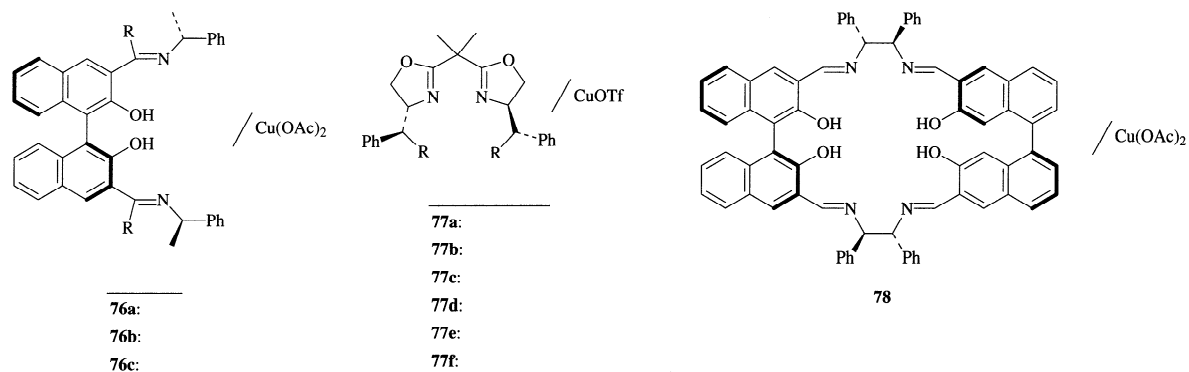
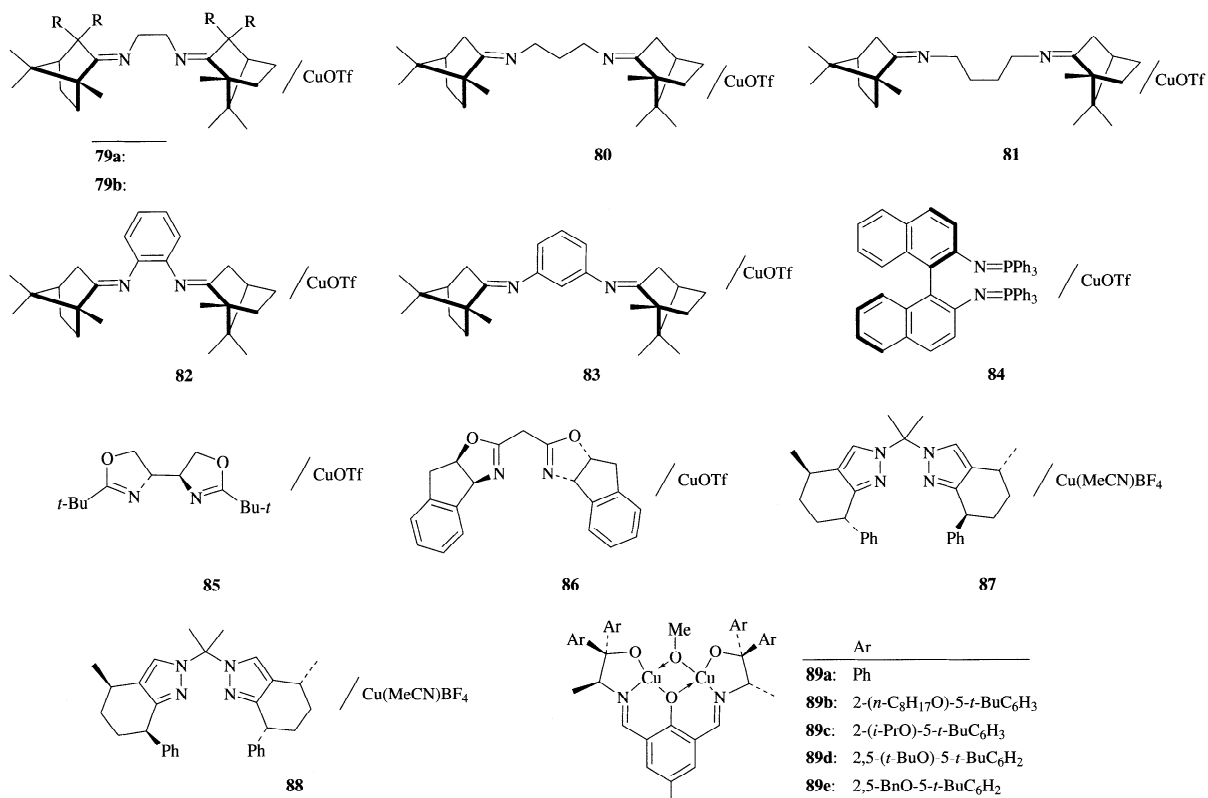


CHART 2. CHIRAL COPPER C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



54

CHART 3. CHIRAL COPPER NON-C₂-SYMMETRIC CATALYST COMPLEXES

55

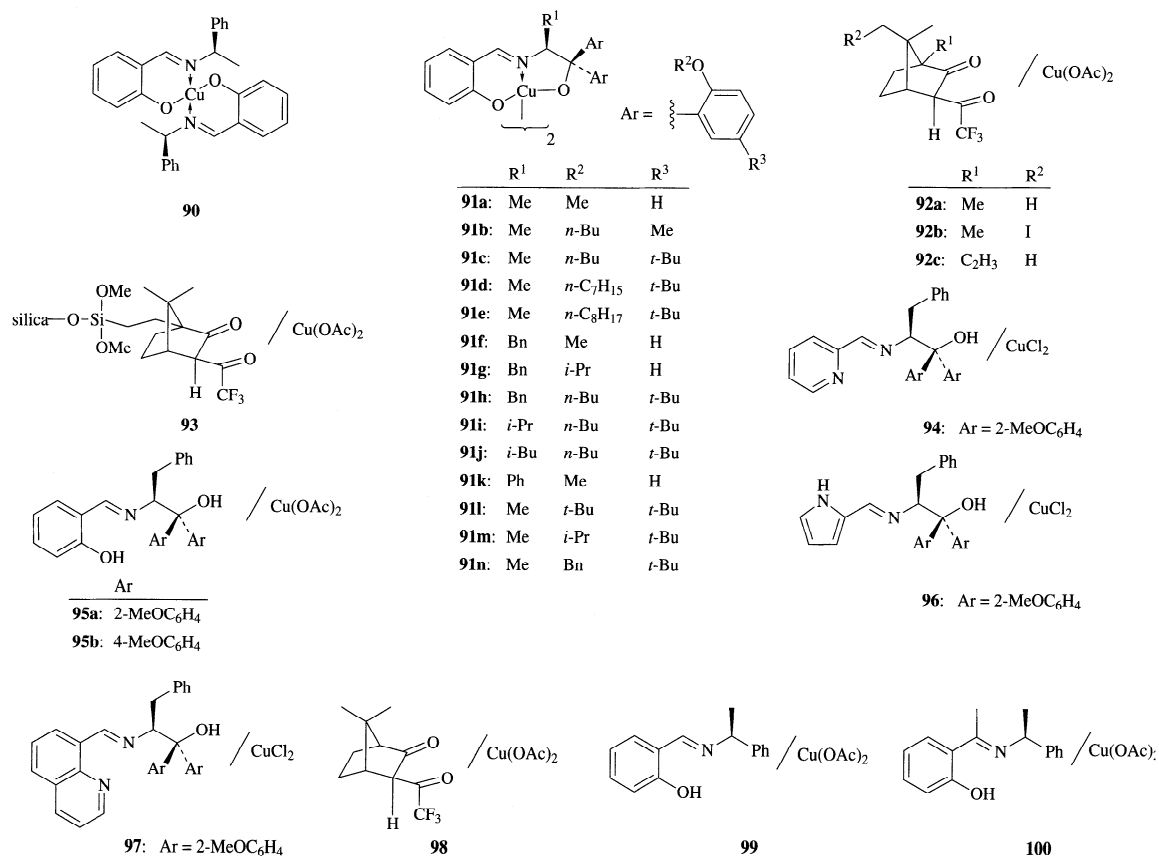


CHART 3. CHIRAL COPPER NON-C₂-SYMMETRIC CATALYST COMPLEXES (Continued)

56

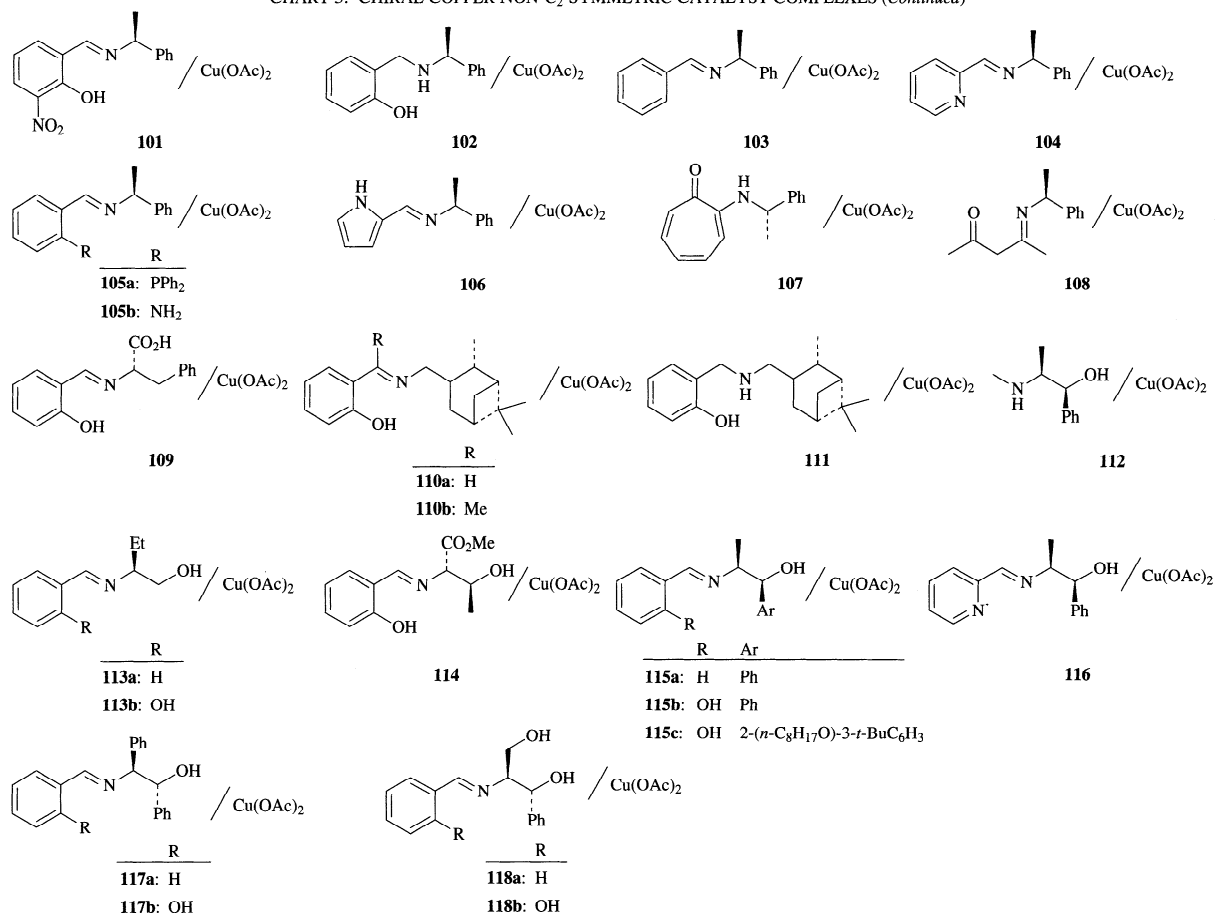
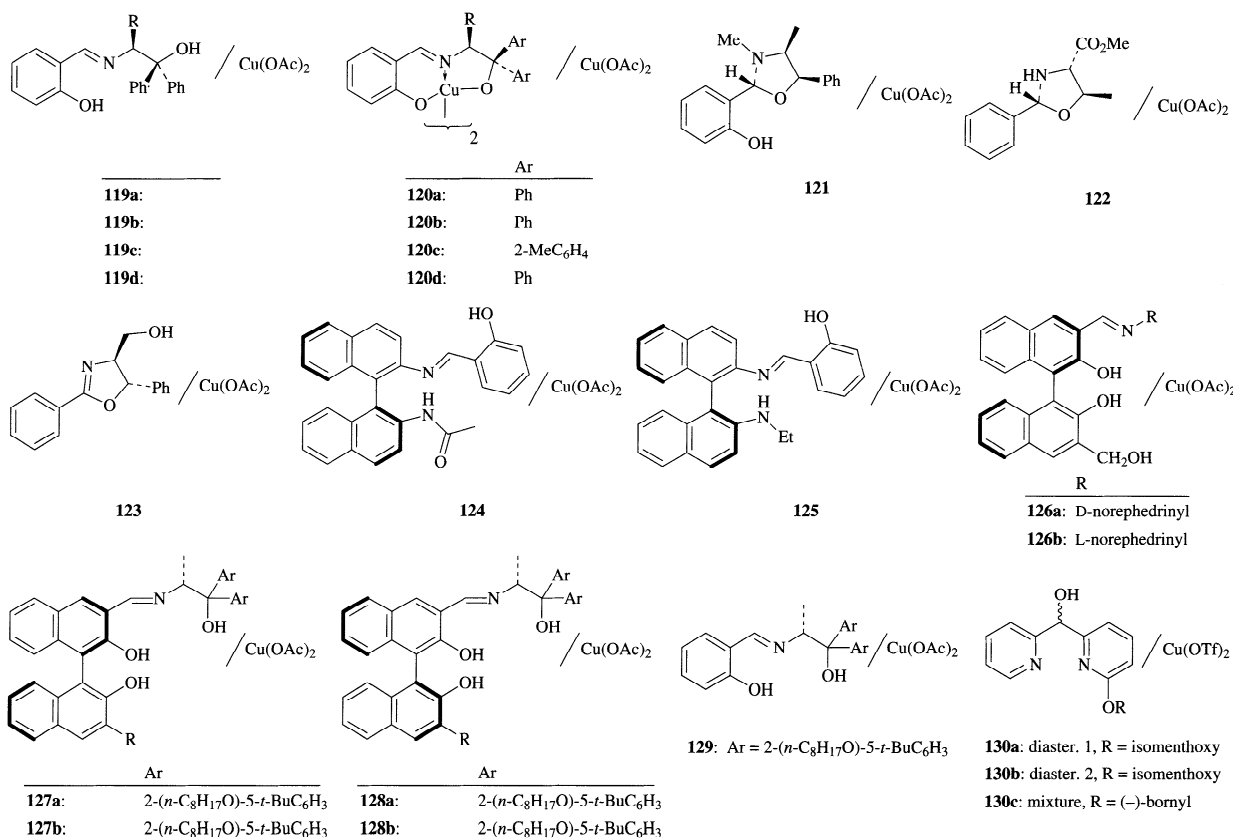
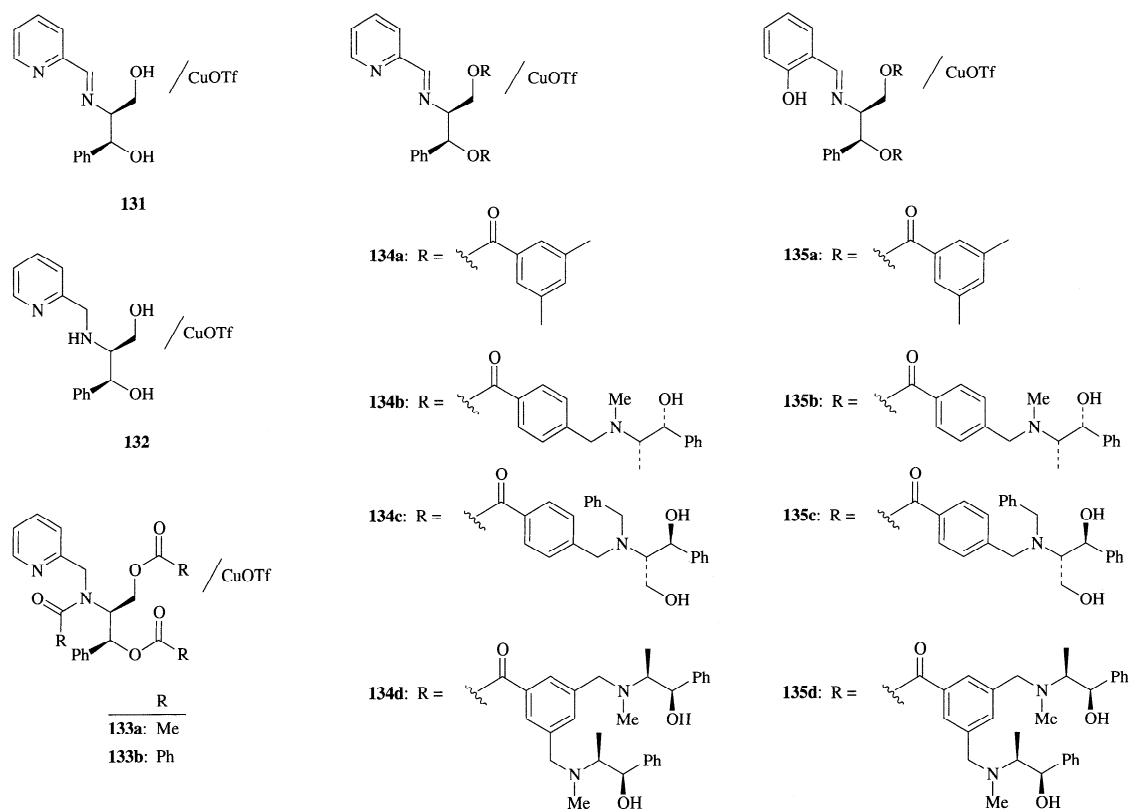


CHART 3. CHIRAL COPPER NON-C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



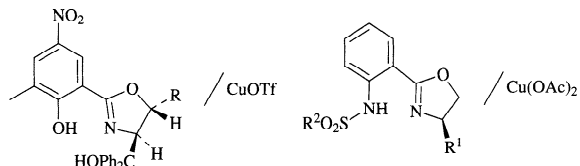
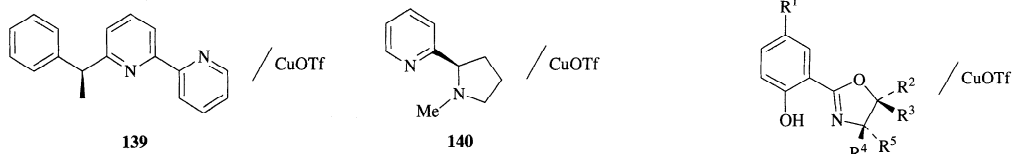
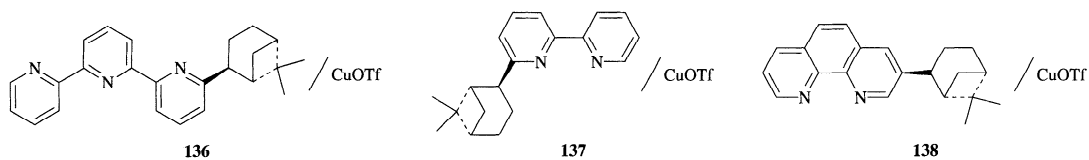
57

CHART 3. CHIRAL COPPER NON-C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



58

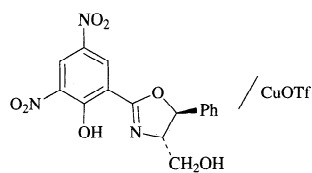
CHART 3. CHIRAL COPPER NON-C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



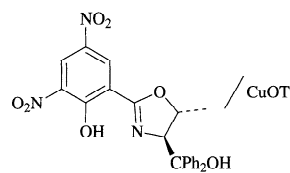
R
142a: H
142b: Me

R ¹	R ²
143a: Ph	4-MeC ₆ H ₄
143b: Ph	1-naphthyl
143c: Ph	2-naphthyl
143d: Ph	2,4,6-Me ₃ C ₆ H ₂
143e: Ph	CF ₃
143f: Ph	4- <i>t</i> -BuC ₆ H ₄
143g: <i>t</i> -Bu	4-MeC ₆ H ₄

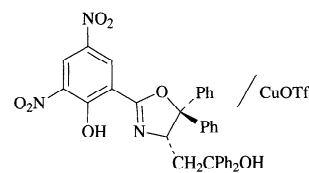
	R ¹	R ²	R ³	R ⁴	R ⁵
141a:	H	H	Ph	H	CH ₂ OH
141b:	H	H	H	CPh ₂ OH	H
141c:	H	Me	H	CPh ₂ OH	H
141d:	H	Ph	Ph	H	CH ₂ C ₆ H ₄ OH-4
141e:	NO ₂	H	Ph	H	CH ₂ OH
141f:	NO ₂	H	H	CPh ₂ OH	H
141g:	NO ₂	Me	H	CPh ₂ OH	H
141h:	NO ₂	Ph	Ph	H	CH ₂ Ph ₂ OH



144

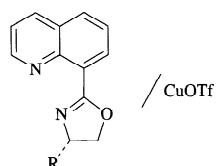


145

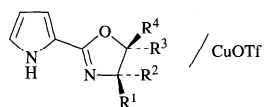


146

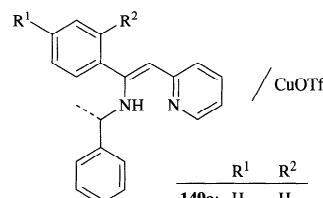
CHART 3. CHIRAL COPPER NON-C₂-SYMMETRIC CATALYST COMPLEXES (Continued)



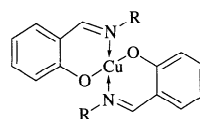
R
147a: Me
147b: Bn
147c: <i>i</i> -Pr
147d: <i>t</i> -Bu
147e: Ph



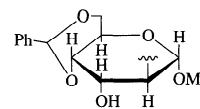
R ¹	R ²	R ³	R ⁴
148a: Me	H	H	H
148b: Et	H	H	H
148c: H	<i>i</i> -Pr	H	H
148d: H	CH(Me)Et	H	H
148e: H	CH ₂ CHMe ₂	H	H
148f: H	<i>t</i> -Bu	H	H
148g: Ph	H	H	H
148h: H	Bn	H	H
148i: H	Me	Ph	H
148j: H	CH ₂ OH	H	Ph
148k: CPh ₂ OH	H	H	H
148l: H	CH ₂ CPh ₂ OH	Ph	Ph



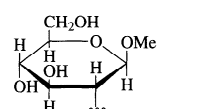
R ¹	R ²
149a: H	H
149b: H	Cl
149c: H	Me
149d: H	Ph
149e: Cl	H
149f: Br	H
149g: Me	H



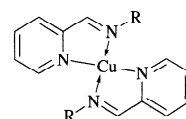
150a: R =



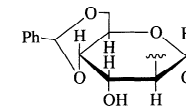
150b: R =



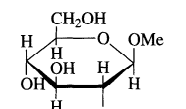
150c: R =



151a: R =



151b: R =



151c: R =

CHART 3. CHIRAL COPPER NON-C₂-SYMMETRIC CATALYST COMPLEXES

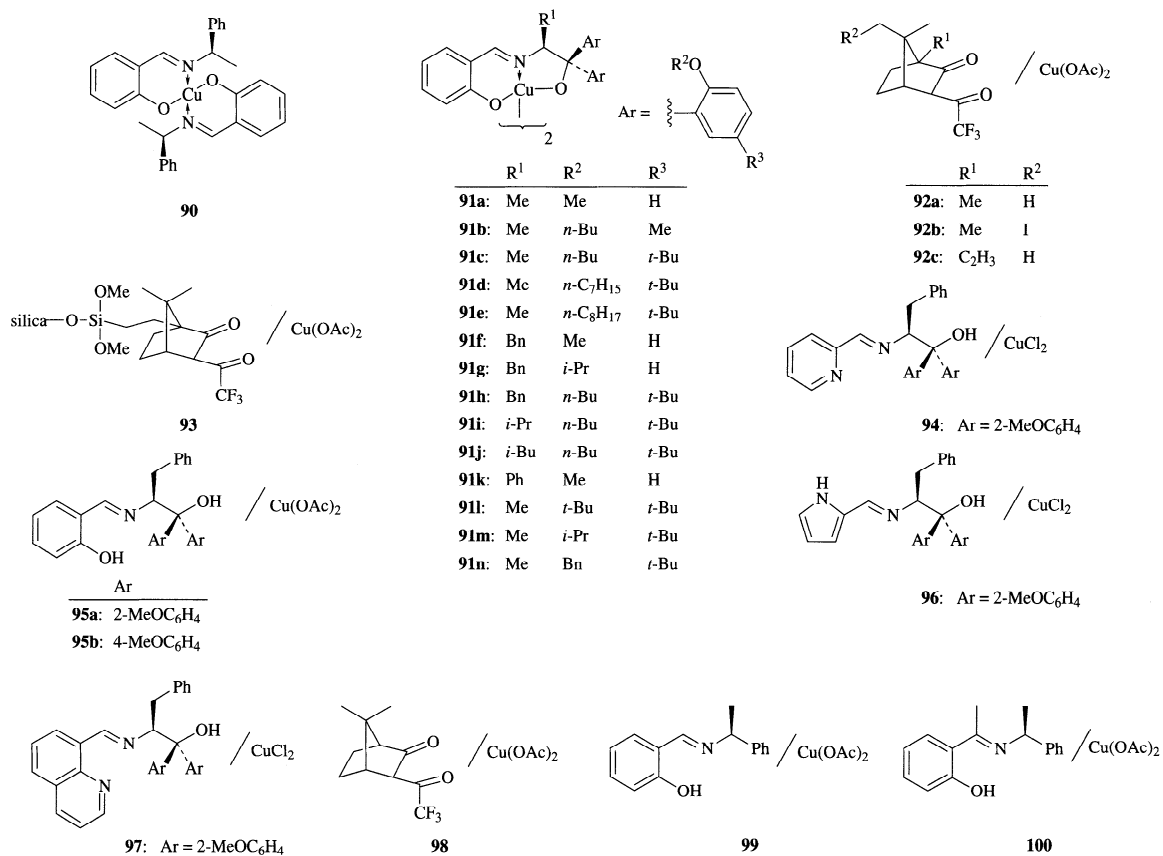
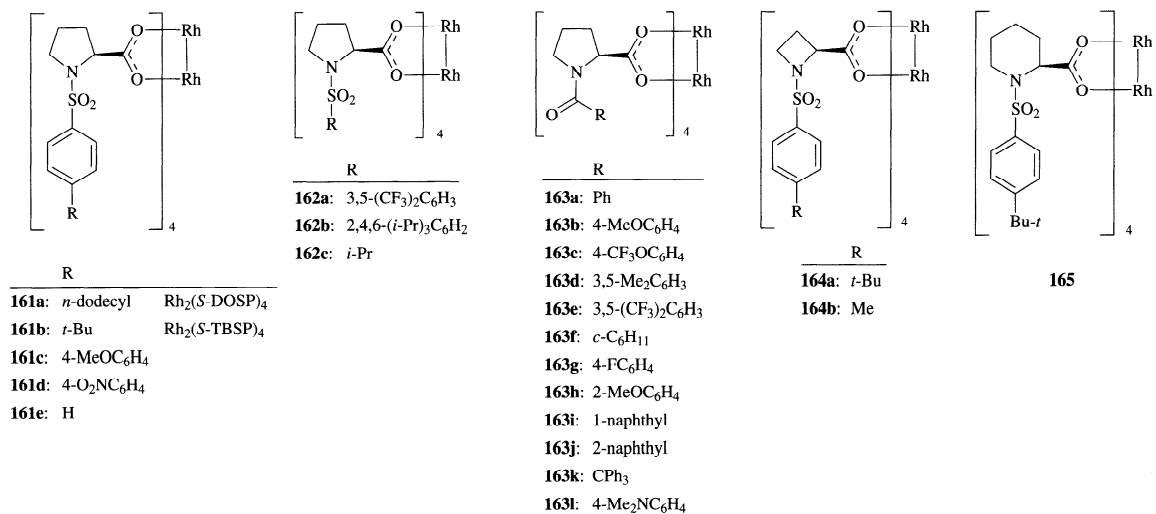


CHART 4. CHIRAL RHODIUM CATALYSTS



62

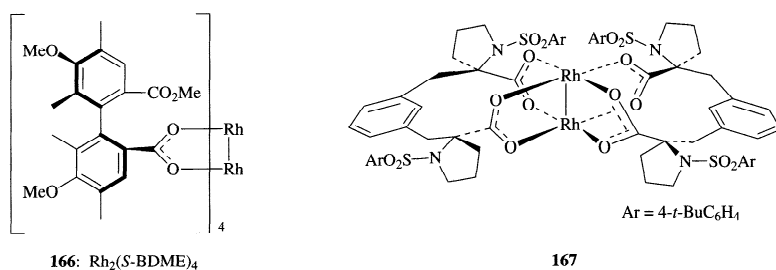
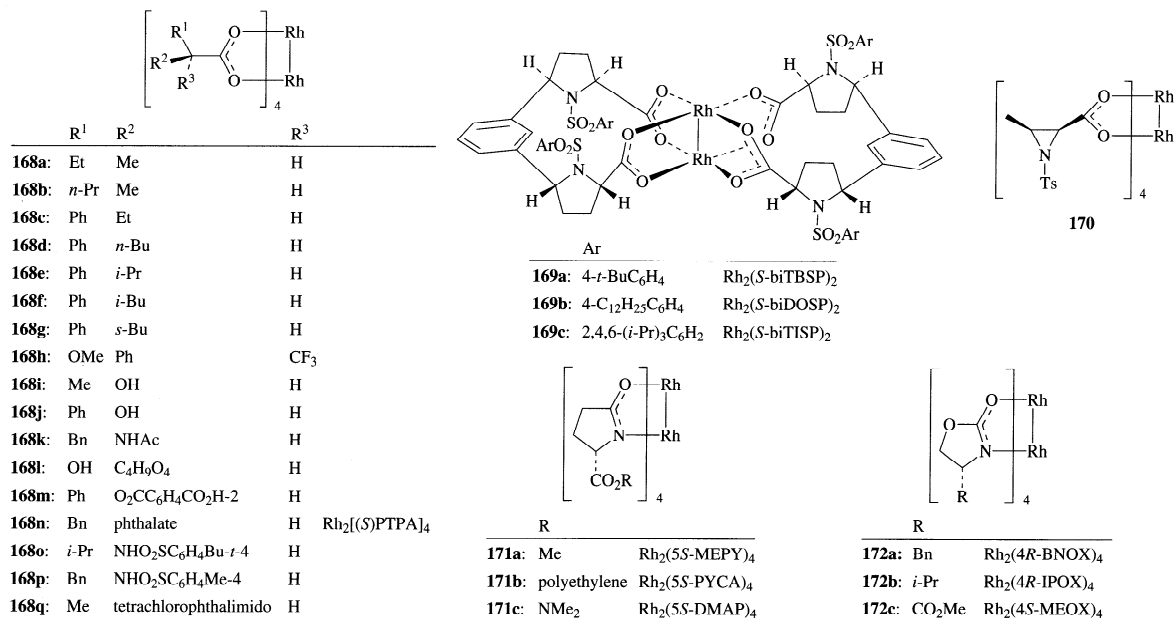
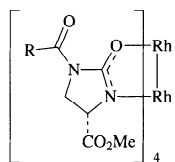


CHART 4. CHIRAL RHODIUM CATALYSTS (Continued)

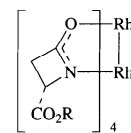
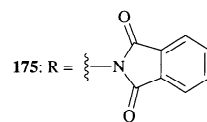
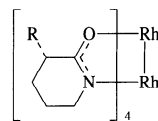


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CHART 4. CHIRAL RHODIUM CATALYSTS (Continued)

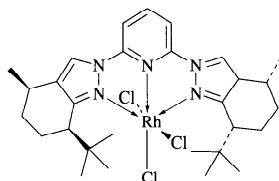


R
174a: Ph Rh₂(4S-MBOIM)₄
174b: 4-*t*-BuC₆H₄ Rh₂(4S-TBOIM)₄



176a: Rh₂(4S-BNAZ)₄
176b: Rh₂(4S-IBAZ)₄

64



177

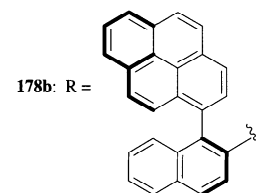
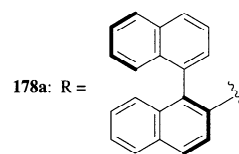
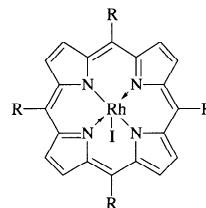
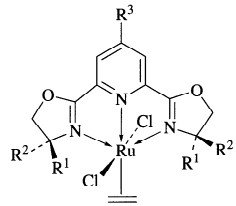
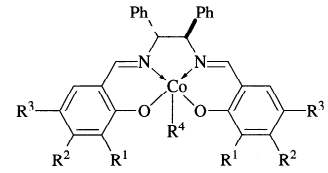
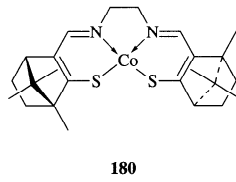
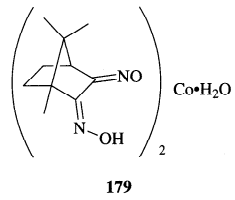
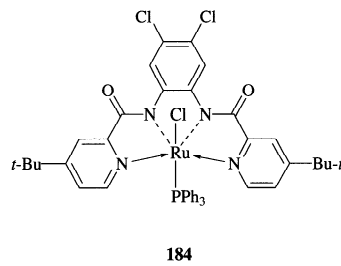
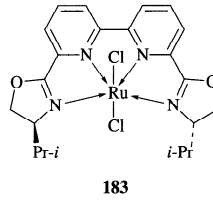


CHART 5. OTHER CHIRAL METAL CATALYSTS



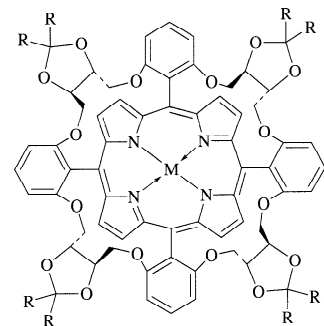
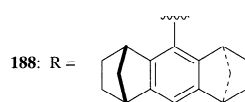
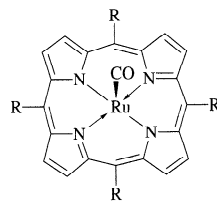
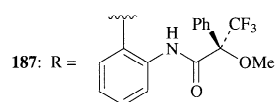
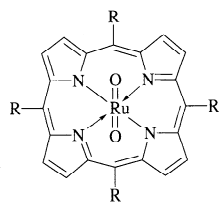
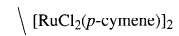
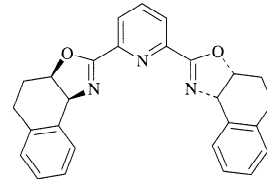
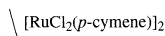
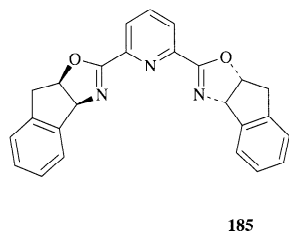
	R ¹	R ²	R ³
182a:	H	Et	H
182b:	<i>s</i> -Bu	H	H
182c:	Bz	H	H
182d:	H	Ph	H
182e:	<i>i</i> -Pr	H	NMe ₂
182f:	<i>i</i> -Pr	H	OMe
182g:	<i>i</i> -Pr	H	H
182h:	<i>i</i> -Pr	H	Cl
182i:	<i>i</i> -Pr	H	CO ₂ Me



	R ¹	R ²	R ³	R ⁴
181a:	<i>t</i> -Bu	H	H	I
181b:	<i>t</i> -Bu	H	H	Br
181c:	<i>t</i> -Bu	H	<i>t</i> -Bu	I
181d:	<i>t</i> -Bu	H	<i>t</i> -Bu	Br
181e:	Me	H	H	I
181f:	H	<i>t</i> -Bu	H	I
181g:	H	<i>t</i> -Bu	H	Br
181h:	H	H	<i>t</i> -Bu	I
181i:	H	H	<i>t</i> -Bu	Br
181j:	H	H	H	I
181k:	H	H	H	Br
181l:	H	H	OMe	Br

65

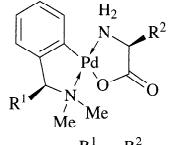
CHART 5. OTHER CHIRAL METAL CATALYSTS (Continued)



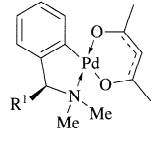
	R	M
189a:	Me	Ru
189b:	Me	Rh
189c:	Me	Fe
189d:	Ph	Ru

66

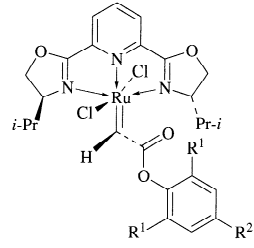
CHART 5. OTHER CHIRAL METAL CATALYSTS (Continued)



	R ¹	R ²
190a:	H	Me
190b:	H	Bz
190c:	H	<i>i</i> -Pr
190d:	Me	H
190e:	Me	Me
190f:	Me	Bz
190g:	Me	<i>i</i> -Pr

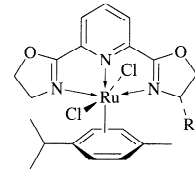


191



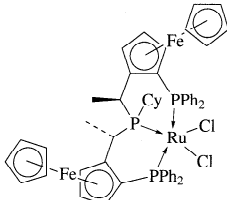
192a: R¹ = Me, R² = Me

192b: R¹ = *i*-Pr, R² = H

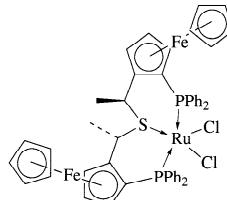


193a: R = *i*-Pr

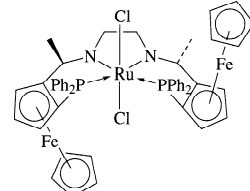
193b: R = *t*-Bu



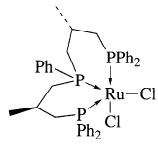
194



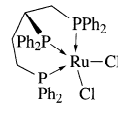
195



196



197



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TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>(See Chart 1 for catalyst structures.)</i>				
C ₁			(4)	288
			(14) <i>exo:endo</i> = 67:33	288
			(15)	288
C ₂			(64)	289
C ₄			(0)	290
	R = Et		(0)	290
			(32) (1)	290 290
			(2)	290
			(76) (20)	290 290
			(62)	290
			(95) <i>trans:cis</i> = 58:42	291
			(73)	292
C ₃	R = Me		(80)	
			(65)	
			(67)	
				293
C ₄	R = Et		(92)	
			(—)	
			(—)	

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

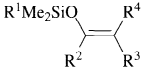
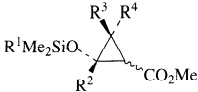
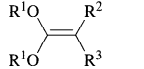
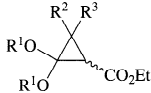
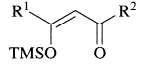
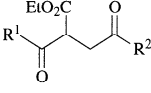
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	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Solvent</th> <th colspan="2"><i>trans:cis</i></th> </tr> </thead> <tbody> <tr><td>Me</td><td>H</td><td>H</td><td>H</td><td>benzene</td><td>(58)</td><td>72:28</td></tr> <tr><td>Me</td><td>H</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(45)</td><td>72:28</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>H</td><td>benzene</td><td>(65)</td><td>65:35</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(70)</td><td>65:35</td></tr> <tr><td>Me</td><td><i>n</i>-C₅H₁₁</td><td>H</td><td>H</td><td>benzene</td><td>(81)</td><td>61:39</td></tr> <tr><td>Me</td><td><i>i</i>-Pr</td><td>H</td><td>H</td><td>benzene</td><td>(68)</td><td>58:42</td></tr> <tr><td>Me</td><td><i>i</i>-Pr</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(80)</td><td>58:42</td></tr> <tr><td>Me</td><td><i>t</i>-Bu</td><td>H</td><td>H</td><td>benzene</td><td>(87)</td><td>52:48</td></tr> <tr><td>Me</td><td><i>t</i>-Bu</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(85)</td><td>52:48</td></tr> <tr><td><i>t</i>-Bu</td><td><i>t</i>-Bu</td><td>H</td><td>H</td><td>benzene</td><td>(69)</td><td>58:42</td></tr> <tr><td><i>t</i>-Bu</td><td><i>t</i>-Bu</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(80)</td><td>58:42</td></tr> <tr><td>Me</td><td>vinyl</td><td>H</td><td>H</td><td>benzene, 100°</td><td>(60)</td><td>64:36</td></tr> <tr><td>Me</td><td>vinyl</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(39)</td><td>64:36</td></tr> <tr><td>Me</td><td>Ph</td><td>H</td><td>H</td><td>benzene</td><td>(75)</td><td>52:48</td></tr> <tr><td>Me</td><td>Ph</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(78)</td><td>52:48</td></tr> <tr><td><i>t</i>-Bu</td><td>Ph</td><td>H</td><td>H</td><td>benzene</td><td>(78)</td><td>60:40</td></tr> <tr><td><i>t</i>-Bu</td><td>Ph</td><td>H</td><td>H</td><td>ethyl acetate</td><td>(77)</td><td>60:40</td></tr> <tr><td>Me</td><td>Ph</td><td>H</td><td>Me</td><td>benzene</td><td>(71)</td><td>55:45</td></tr> <tr><td>Me</td><td>Ph</td><td>H</td><td>Me</td><td>ethyl acetate</td><td>(71)</td><td>55:45</td></tr> <tr><td>Me</td><td>Ph</td><td>Me</td><td>Me</td><td>benzene</td><td>(72)</td><td>54:46</td></tr> <tr><td>Me</td><td>Ph</td><td>Me</td><td>Me</td><td>ethyl acetate</td><td>(80)</td><td>54:46</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>benzene</td><td>(86)</td><td>68:32</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>ethyl acetate</td><td>(77)</td><td>68:32</td></tr> <tr><td>Me</td><td>H</td><td>Me</td><td>Me</td><td>benzene</td><td>(79)</td><td>75:25</td></tr> <tr><td>Me</td><td>H</td><td>Me</td><td>Me</td><td>ethyl acetate</td><td>(67)</td><td>75:25</td></tr> <tr><td></td><td><i>t</i>-Bu</td><td>H</td><td>Me</td><td>Me</td><td>benzene</td><td>(77)</td><td>77:23</td></tr> <tr><td></td><td>Me</td><td>H</td><td>H</td><td>Me</td><td>benzene</td><td>(73)</td><td>78:22</td></tr> <tr><td></td><td>Me</td><td>H</td><td>H</td><td>Me</td><td>ethyl acetate</td><td>(70)</td><td>78:22</td></tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Solvent	<i>trans:cis</i>		Me	H	H	H	benzene	(58)	72:28	Me	H	H	H	ethyl acetate	(45)	72:28	Me	Me	H	H	benzene	(65)	65:35	Me	Me	H	H	ethyl acetate	(70)	65:35	Me	<i>n</i> -C ₅ H ₁₁	H	H	benzene	(81)	61:39	Me	<i>i</i> -Pr	H	H	benzene	(68)	58:42	Me	<i>i</i> -Pr	H	H	ethyl acetate	(80)	58:42	Me	<i>t</i> -Bu	H	H	benzene	(87)	52:48	Me	<i>t</i> -Bu	H	H	ethyl acetate	(85)	52:48	<i>t</i> -Bu	<i>t</i> -Bu	H	H	benzene	(69)	58:42	<i>t</i> -Bu	<i>t</i> -Bu	H	H	ethyl acetate	(80)	58:42	Me	vinyl	H	H	benzene, 100°	(60)	64:36	Me	vinyl	H	H	ethyl acetate	(39)	64:36	Me	Ph	H	H	benzene	(75)	52:48	Me	Ph	H	H	ethyl acetate	(78)	52:48	<i>t</i> -Bu	Ph	H	H	benzene	(78)	60:40	<i>t</i> -Bu	Ph	H	H	ethyl acetate	(77)	60:40	Me	Ph	H	Me	benzene	(71)	55:45	Me	Ph	H	Me	ethyl acetate	(71)	55:45	Me	Ph	Me	Me	benzene	(72)	54:46	Me	Ph	Me	Me	ethyl acetate	(80)	54:46	Me	Me	Me	Me	benzene	(86)	68:32	Me	Me	Me	Me	ethyl acetate	(77)	68:32	Me	H	Me	Me	benzene	(79)	75:25	Me	H	Me	Me	ethyl acetate	(67)	75:25		<i>t</i> -Bu	H	Me	Me	benzene	(77)	77:23		Me	H	H	Me	benzene	(73)	78:22		Me	H	H	Me	ethyl acetate	(70)	78:22		
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TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
R = Et		Cu(acac) ₂ , CH ₂ Cl ₂ , 60°, 3 d		297																		
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R ¹	R ²	R ³																				
OEt	Mc	Mc																				
OEt	Me	H																				
Me	Me	Me																				
Me	Me	H																				
Me	H	Me																				
R = Et		Cu(OTf) ₂ , benzene, 0°		95																		
	NC-CH=CH ₂	Mo(CO) ₆ , neat, rt, 72 h Mo(CO) ₆ , neat, 65°, 7 h Mo ₂ (OAc) ₄ , neat, 65°	 <i>trans:cis</i> (46) 58:42 (46) 52:48 (42) 52:48	298 298, 299 299																		
C ₃ R = Me		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	 <i>trans:cis</i> (67) 66:34 (68) 60:40 (26) —	300																		
	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> </tr> </tbody> </table>	R ¹	R ²	R ³	H	H	H	Me	H	H	H	Me	Me									
R ¹	R ²	R ³																				
H	H	H																				
Me	H	H																				
H	Me	Me																				
		CuO, 150°		301																		
	R = Me		(47)																			
C ₄	R = Et		(33)																			
C ₆	R = Bu		(18)																			
C ₄	R = Et		 <i>trans:cis</i> (55) 52:48 (30) 52:48 (7) 64:36	71, 302 71 71, 302																		
	R = Et		 <i>trans:cis</i> (90) 55:45 (24) 55:45 (50) 64:36	71, 302 71 71, 302																		
	R = Et		Rh ₂ (OAc) ₄		303																	
		Rh ₂ (OAc) ₄ , neat, rt, 4 h		(68) <i>trans:cis</i> = 57:43	304																	
	R = Et		CuSO ₄ , neat, 95°		(38) <i>trans:cis</i> = 58:42	305																
	R = Et																					

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	R = Me 	Cu(acac) ₂ , DCE, 80°	 (77) <i>trans:cis</i> = 85:15	300
C ₄	R = Et 	Mo(CO) ₆ , neat, rt, 72 h Mo(CO) ₆ , neat, 65°, 3 h Mo ₂ (OAc) ₄ , neat, 65° Mo(CO) ₆ , benzene, 65° Mo(CO) ₄ (PPh ₃) ₂ , benzene, 65° Mo(CO) ₄ (pip) ₂ , benzene, 65° Mo(CO) ₄ (PPh ₃)(pip), benzene, 65° Mo(N ₂) ₂ (dppe) ₂ , benzene, 65°	 <i>trans:cis</i> (77) 41:59 (79) 41:59 (72) 44:56 (80) — (81) — (0) — (63) — (15) —	298 298, 299 299 299 299 299 299 299
	R = Et 	CuOTf, cyclohexane, 0°, 8 h	 (64) <i>exo:endo</i> = 80:20	306
C ₃	R = Me 	Cu(acac) ₂ , 100°, 3 h [Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , rt	 (51) (62) <i>trans:cis</i> = >97:3	307 308
	R = Me 	Cu(acac) ₂ , 100°, 3 h	 (26)	307
C ₄	R Et Et 	Pd(OAc) ₂ , benzene, 40° Mo ₂ (OAc) ₄ , neat, 65°	 <i>trans:cis</i> (76) 80:20 (32) 60:40	79 299
	R Me Et Et Et Et Et Et Et Ph 	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt Rh ₂ (OAc) ₄ , neat, rt Rh ₂ (OAc) ₄ , neat, rt Cu(OTf) ₂ , neat, rt Pd(OAc) ₂ , neat, rt Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60° Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60° ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60° Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	 <i>trans:cis</i> (60) 63:37 (77) — (59) 62:38 (22) — (5) — (81) 57:43 (34) 62:38 (88) 56:44 (42) 65:35 (44) 60:40	309 80 71 80 80 51 51 51 309 309
C ₄	R = Et 	Pd(OAc) ₂ , benzene, 40°	 (64) <i>trans:cis</i> = 69:31	79
	R = Et 	Cu-bronze, 80°	 (80)	95
	R = Et 	1. CuSO ₄ , 90° 2. KOH, MeOH, rt	 (45)	310

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		Cu, cyclohexane, 80°	(60)	311
C ₃	R = Me 	Cu(acac) ₂ , benzene, 90°	(66)	312
		Cu(acac) ₂ , EtOAc, 100°	(81) <i>trans:cis</i> = 75:25	313
C ₄	R = Et 	Rh ₂ (OAc) ₄ , neat, rt	(25) <i>trans:cis</i> = 69:31	71
R = Et		Pd(OAc) ₂ , Et ₂ O, rt	(88)	314
C ₃	R 	Rh ₂ (OAc) ₄ , neat, rt	(54)	80
		Pd(OAc) ₂ , neat, rt	(24)	80
C ₄	Et 	Cu(OTf) ₂ , Et ₂ O, reflux, 6 h	(33)	315
		CuOTf, 0°	(>50)	316
C ₃	R 	Pd(OAc) ₂ , neat, rt	(21)	80
		CuOTf, 0°	(>50)	316
R = Et		[Cu(MeCN) ₄] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , rt, 20 min	(71)	317
C ₃ C ₄	R 	Cu(acac) ₂ , 100°, 3 h	(52) —	307
		Rh ₂ (OAc) ₄ , neat, rt	(78) 50:50	71
		Rh ₂ (OAc) ₄ , Et ₂ O, rt	(65) 70:30	94
		Rh ₆ (CO) ₁₆ , Et ₂ O, rt	(63) 67:33	94
		Rh ₆ (CO) ₁₆ , neat, rt	(72) 50:50	71, 318
		PdCl ₂ •PhCN, neat, rt	(66) —	318
		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(67) 52:48	71, 358
		CuCl•P(OPr- <i>i</i>) ₃ , Et ₂ O, rt	(40) 71:29	94
		MeReO ₃ , neat	(69) —	319
		Cu-bronze, neat, reflux, 19 h	(60) —	320
		(CO) ₅ WC(OMe)Ph, 35°	(70) 47:53	321
		PdCl ₂ •2PhCN, neat, rt	(66) 48:52	71
		[(Cp)Fe(CO) ₂ (THF)] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , 40°	(66) 45:55	322

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)


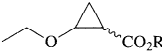
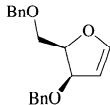
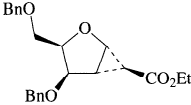
Carbenoid Precursor		Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
						
	R			<i>trans:cis</i>		
C ₃	Me		[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , rt	(89)	82:18	308
	Me		Ru ₂ (CO) ₄ (μ-OAc) ₂ (MeCN) ₂ , CH ₂ Cl ₂ , rt	(54)	92:8	308
	Me		Ru ₂ (CO) ₄ (μ-OAc) ₂ (MeCN) ₂ , neat, 36°	(83)	84:16	308
C ₄	Et		CuCl•P(OPh) ₃ , neat, rt	(64)	69:31	71
	Et		Cu(OTf) ₂ , neat, 0°	(55)	71:29	71
	Et		Cu(acac) ₂ , neat, rt	(15)	62:38	71
	Et		Rh ₂ (OAc) ₄ , Et ₂ O, rt	(75)	62:38	94
	Et		Rh ₂ (OAc) ₄ , rt	(60-93)	62:38	323
	Et		Rh ₂ (O ₂ CC ₃ F ₇ - <i>n</i>) ₄ , rt	(60-93)	57:43	323
	Et		Rh ₂ (NHCOCH ₃) ₄ , rt	(60-93)	74:26	323
	Et		Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(72)	<i>trans</i>	78
	Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(62)	<i>trans</i>	78
	Et		Rh ₂ (O ₂ CC ₃ H ₇) ₄ , CH ₂ Cl ₂ , rt, 5 h	(60)	<i>trans</i>	78
	Et		Rh ₂ (NHCOCF ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(62)	<i>trans</i>	78
	Et		Rh ₂ (OCSCCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(60)	<i>trans</i>	78
	Et		Rh ₂ (O ₂ CCF ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(59)	<i>trans</i>	78
	Et		Rh ₂ (O ₂ CC ₃ F ₇ - <i>n</i>) ₄ , CH ₂ Cl ₂ , rt, 5 h	(57)	<i>trans</i>	78
	Et		Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(72)	<i>trans</i>	78
	Et		Rh ₂ (OAc) ₄ , neat, rt	(88)	63:37	71
	Et		Rh ₆ (CO) ₁₆ , neat, rt	(62)	63:37	71
	Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(61)	66:34	71
	Et		PdCl ₂ •2PhCN, neat, rt	(43)	60:40	71
	Et		Rh ₂ (OAc) ₄ , neat, rt	(85)	—	80
	Et		Cu(OTf) ₂ , neat, rt	(0)	—	80
	Et		Pd(OAc) ₂ , neat, rt	(42)	—	80
	Et		Rh ₆ (CO) ₁₆ , neat, rt	(62)	—	318
	Et		PdCl ₂ •PhCN, neat, rt	(43)	—	318
	Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(61)	—	318
	Et		Iron meso-tetra(pentafluorophenyl) porphyrin chloride, CH ₂ Cl ₂ , rt, 4 h	(—)	77:23	57
	Et		Iron meso-tetramesitylporphyrin chloride/cobaltocene, CH ₂ Cl ₂ , rt, 4 h	(—)	80:20	57
	Et		Iron octaethylporphyrin chloride/cobaltocene, CH ₂ Cl ₂ , rt, 4 h	(—)	82:18	57
	Et		(CO) ₅ WC(OMe)Ph, 35°	(38)	58:42	321
	Et		[(Cp)Fe(CO) ₂ (THF)] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , 40°	(66)	55:45	322
C ₁₀	2,3,4-Me ₃ -3-pentyl		Rh ₂ (OAc) ₄ , rt	(62-99)	70:30	323
	2,3,4-Me ₃ -3-pentyl		Rh ₂ (O ₂ CC ₃ F ₇ - <i>n</i>) ₄ , rt	(62-99)	60:40	323
	2,3,4-Me ₃ -3-pentyl		Rh ₂ (NHCOCH ₃) ₄ , rt	(62-99)	81:19	323
	2,3,4-Me ₃ -3-pentyl		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(67)	<i>trans</i>	78
	2,3,4-Me ₃ -3-pentyl		Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(80)	<i>trans</i>	78
C ₁₂	<i>d</i> -menthyl		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	(88)	63:37	359
	3- <i>i</i> -Pr-2-Me-3-heptyl		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(70)	<i>trans</i>	78
C ₁₃	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(71)	<i>trans</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂		Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(85)	<i>trans</i>	78
C ₄	R = Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 1 h		(52)	324

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

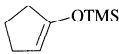
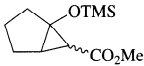
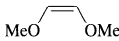
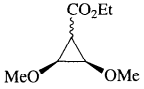



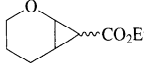

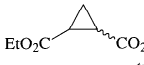

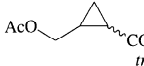

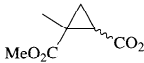
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	R = Me 	Cu(acac) ₂ , benzene, 100°	 (72) <i>trans:cis</i> = 54:46	294, 312
C ₄	R = Et 	Cu-bronze, 80°	 (83)	95
	R 		 <i>exo:endo</i>	
	Et	Rh ₂ (O ₂ CH) ₄ , 60°	(—) 62:38	325
	Et	Rh ₂ (OAc) ₄ , 60°	(—) 71:29	325
	Et	Rh ₂ (O ₂ CBu- <i>n</i>) ₄ , 60°	(—) 71:29	325
	Et	Rh ₂ (OAc) ₄ , neat, rt	(95) —	80
	Et	Rh ₂ (OAc) ₄ , neat, rt	(96) 68:32	71
	Et	Cu(OTf) ₂ , neat, rt	(60) —	80
	Et	Pd(OAc) ₂ , neat, rt	(60) —	80
	Et	Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(49) 51:49	51
	Et	Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(26) 51:49	51
	Et	ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(53) 50:50	51
	Et	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(72) <i>exo</i>	78
	Et	CuOTf, DCE, rt	(61) 77:23	326
	Et	4, DCE, rt	(64) 94:6	326
	Et	5, DCE, rt	(66) 97:3	326
	Et	6, DCE, rt	(51) 98:2	326
C ₁₃	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(97) <i>exo</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(69) <i>exo</i>	78
	R 		 <i>exo:endo</i>	
C ₄	Et	Rh ₂ (OAc) ₄ , neat, rt	(71) —	80
	Et	Rh ₂ (OAc) ₄ , neat, rt	(91) 87:13	71
	Et	Cu(OTf) ₂ , neat, rt	(55) —	80
	Et	Pd(OAc) ₂ , neat, rt	(20) —	80
	Et	Rh ₆ (CO) ₁₆ , neat, rt	(82) 87:13	71, 318
	Et	PdCl ₂ •PhCN, neat, rt	(41) 79:21	71, 318
	Et	CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(18) 86:14	71, 318
	Et	(CO) ₅ WC(OMe)Ph, 35°	(32) 84:16	321
	Et	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(87) <i>exo</i>	78
C ₁₃	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(85) <i>exo</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(97) <i>exo</i>	78
	R 		 <i>trans:cis</i>	
C ₄	Et	Mo(CO) ₆ , neat, rt, 72 h	(36) 60:40	298
	Et	Mo(CO) ₆ , neat, 65°, 8 h	(31) 62:38	298, 299
	Et	Mo ₂ (OAc) ₄ , neat, 65°	(27) 60:40	299
	Et	Pd(OAc) ₂ , benzene, 40°	(64) 69:31	79
	R 	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	 <i>trans:cis</i>	309
C ₃	Me		(57) 59:41	
C ₁₂	<i>l</i> -menthyl		(49) 68:32	
	R 		 <i>trans:cis</i>	
C ₄	Et	Mo(CO) ₆ , neat, 65°	(80) 58:42	299
	Et	Mo ₂ (OAc) ₄ , neat, 65°	(71) 58:42	299
	Et	Pd(OAc) ₂ , benzene, 40°	(30) 55:45	79

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		CuSO ₄ , 75°	(—)	327
R = Et		CuSO ₄ , neat, 90°, 10 h	(28)	328
R = Et		CuSO ₄ , neat, 90°, 10 h	(24)	328
R = Et		Rh ₂ (OAc) ₄ , neat, rt	(58) <i>trans:cis</i> = 67:33	71
R = Et		Rh ₂ (OAc) ₄ , neat, rt [(Cp)Fe(CO) ₂ (THF)] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , 40°	(25) <i>trans:cis</i> = 69:31 (0)	71 322
R		Rh ₂ (OAc) ₄ , neat, rt	(70) —	80
Et		Cu(OTf) ₂ , neat, rt	(30) —	80
Et		Pd(OAc) ₂ , neat, rt	(5) —	80
Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(60) <i>trans</i>	78
Et		Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(58) <i>trans</i>	78
C ₁₀	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(64) <i>trans</i>	78
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(66) <i>trans</i>	78
C ₁₃	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(65) <i>trans</i>	78
	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(65) <i>trans</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(96) <i>trans</i>	78
R		Rh ₂ (OAc) ₄ , rt	<i>trans:cis</i>	
C ₄	Et	Rh ₂ (OAc) ₄ , rt	(60-93) 63:37	323
	Et	Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(60-93) 57:43	323
	Et	Rh ₂ (NHCOCH ₃) ₄ , rt	(60-93) 74:26	323
C ₁₀	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , rt	(62-99) 68:32	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(62-99) 58:42	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (NHCOCH ₃) ₄ , rt	(62-99) 79:21	323
C ₃	R = Me	Cu(acac) ₂ , 100°, 3 h	(83)	307
			(29)	
C ₃	Me	Cu(acac) ₂ , 100°, 3 h	(29)	307
C ₄	Et	Cu-bronze, methylcyclohexane, reflux, 4 h	(—) <i>trans:cis</i> = 70:30	329


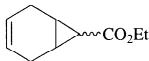


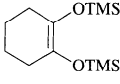
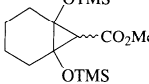
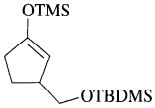
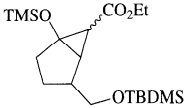
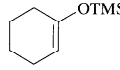
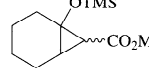
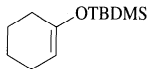
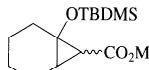
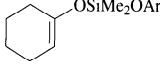
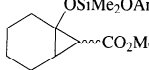
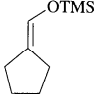
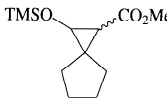

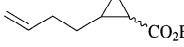
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TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																										
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R = Et		CuSO ₄ , 65°	(19)	330																																																																																										
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TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R				
Et		Rh ₂ (OAc) ₄ , neat, rt, 10 h	(80) —	77
Et		Cu(OTf) ₂ , neat, rt, 10 h	(60) —	77
Et		Pd(OAc) ₂ , neat, rt, 10 h	(37) —	77
Et		Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(61) 29:71	51
Et		Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(34) 31:69	51
Et		ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(63) 29:71	51
R = Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 0°, 12 h	 (77)	333
C ₃	R = Me 	Cu(acac) ₂ , solvent, reflux		
		Solvent	<i>trans:cis</i>	
		benzene	(63) >95:5	294, 312
		ethyl acetate	(66) >95:5	294
C ₄	R = Et 	Cu(acac) ₂ , benzene, reflux	 (75)	334
C ₃	R = Me 	Cu(acac) ₂ , solvent, reflux		
		Solvent	<i>trans:cis</i>	
		benzene	(75) 42:58	294, 312
		ethyl acetate	(71) 42:58	294
R = Me		Cu(acac) ₂ , ethyl acetate, reflux	 (64) <i>trans:cis</i> = 50:50	294
R = Me		Cu(acac) ₂ , ethyl acetate, reflux	 (89) <i>trans:cis</i> = 55:45	294
R = Me		Cu(acac) ₂ , benzene, reflux	 (58) <i>trans:cis</i> = 75:25	294
C ₄	R = Et 	Catalyst, neat, rt		80
		Catalyst		
		Rh ₂ (OAc) ₄	(80)	
		Cu(OTf) ₂	(60)	
		Pd(OAc) ₂	(37)	

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TABLE I. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)


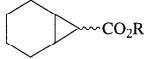
Carbenoid Precursor		Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
						
	R			<i>exo:endo</i>		
C ₃	Me		Cu(acac) ₂ , 100°, 3 h	(62)	—	307
	Mc		Rh ₂ (OAc) ₄ , neat, rt	(80)	—	80
	Me		Rh ₂ (OAc) ₄ , neat, rt, 10 h	(84)	—	77
	Me		Rh ₂ (O ₂ CC ₃ H _{7-n}) ₄ , neat, rt, 10 h	(85)	—	77
	Me		Cu(OTf) ₂ , neat, rt, 10 h	(54)	—	77
	Me		[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , rt	(68)	79:21	308
	Mc		Pd(OAc) ₂ , neat, rt	(15)	—	80
C ₄	Et		MeReO ₃ , neat	(71)	—	319
	Et		Rh ₂ (OAc) ₄ , rt	(60-93)	79:21	323
	Et		Rh ₂ (O ₂ CC ₃ F _{7-n}) ₄ , rt	(60-93)	67:33	323
	Et		Rh ₂ (NHCOCH ₃) ₄ , rt	(60-93)	91:9	323
	Et		Iodorhodium(III)- <i>meso</i> -tetraphenylporphyrin, neat, 60°	(62)	54:46	102
	Et		Iodorhodium(III)- <i>meso</i> -tetraphenylporphyrin, CDCl ₃ , 55°	(76)	—	335
	Et		Iodorhodium(III)- <i>meso</i> -tetraphenylporphyrin, DCE, 60°	(62)	57:43	101
	Et		Iodorhodium(III)- <i>meso</i> -tetraphenylporphyrin, DCE, 60°	(83)	46:54	101
	Et		Iodorhodium(III)- <i>meso</i> -cyanooctaethylporphyrin, DCE, 60°	(38)	60:40	101
	Et		Iodorhodium(III)- <i>meso</i> -tetra- <i>o</i> -tolylporphyrin, DCE, 60°	(53)	55:45	101
	Et		[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(14)	61:39	91
	Et		Zeolite NaCuX-38, 83°	(—)	—	336
	Et		Rh ₂ (O ₂ CH) ₄ , 60°	(95)	69:31	325
	Et		Rh ₂ (OAc) ₄ , rt	(83)	79:21	325
	Et		Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , rt	(93)	87:13	325
	Et		Rh ₂ (O ₂ CC ₁₇ H _{35-n}) ₄ , rt	(97)	77:23	325
	Et		Rh ₂ (O ₂ CPh) ₄ , 60°	(96)	72:28	325
	Et		Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 60°	(95)	70:30	325
	Et		Rh ₂ [O ₂ C(CH ₂) ₂ Ph] ₄ , rt	(97)	75:25	325
	Et		Rh ₂ (O ₂ CCH ₂ CPh ₃) ₄ , rt	(96)	62:38	325
Et		Rh ₂ [O ₂ CC ₆ H ₄ OH-2] ₄ , 60°	(91)	65:35	325	
Et		Rh ₂ [O ₂ CC ₆ H ₄ Bz-2] ₄ , rt	(96)	54:46	325	
Et		Rh ₂ [O ₂ C-2,4-Cl ₂ C ₆ H ₃ (NO ₂) _{2-3,5}] ₄ , rt	(30)	48:52	325	
Et		Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -2) ₄ , rt	(98)	64:36	325	
Et		Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -3) ₄ , rt	(98)	83:17	325	
Et		Rh ₂ (O ₂ CC ₆ H ₂ Me ₃ -2,4,6) ₄ , 60°	(91)	67:33	325	
Et		Rh ₂ (O ₂ CC ₂ H ₄ COME) ₄ , rt	(98)	76:24	325	
Et		Rh ₂ (O ₂ CCOPh) ₄ , 60°	(92)	70:30	325	
Et		Rh ₂ (O ₂ CCF ₃) ₄ , rt	(91)	69:31	325	
Et		Rh ₂ (OAc) ₄ , Et ₂ O, rt	(80)	82:18	94	
Et		Rh ₆ (CO) ₁₆ , Et ₂ O, rt	(43)	75:25	94	
Et		Rh ₆ (CO) ₁₆ , neat, rt	(88)	—	318	
Et		Rh ₂ (OAc) ₄ , neat, rt	(88)	—	80	
Et		Cu(OTf) ₂ , neat, rt	(54)	—	80	
Et		Pd(OAc) ₂ , neat, rt	(21)	—	80	
Et		PdCl ₂ •PhCN, neat, rt	(31)	—	318	
Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(28)	—	318	
Et		CuCl•P(OPr- <i>i</i>) ₃ , Et ₂ O, rt	(40)	93:7	94	
Et		CuCl•PMe ₃ , neat, reflux	(77)	—	337	

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Et		RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(4) 73:27	52, 338
Et		RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(5) 77:23	52
Et		RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(3) 75:25	52
Et		Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(4) 72:28	52
Et		(CO) ₅ WC(OMe)Ph, 35°	(33) 78:22	321
Et		Rh ₂ (OAc) ₄ , neat, rt	(90) 79:21	71
Et		Rh ₆ (OAc) ₁₆ , neat, rt	(88) 80:20	71
Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(28) 87:13	71
Et		PdCl ₂ •2PhCN, neat, rt	(31) 69:31	71
Et		CuCl•P(OPh) ₃ , neat, rt	(25) 88:12	71
Et		Cu(OTf) ₂ , neat, rt	(80) 87:13	71
Et		Cu-bronze, neat, rt	(23) 88:12	71
Et		Cu(acac) ₂ , neat, 60°	(18) 87:13	71
Et		Cu-bronze-K10 montmorillonite, CH ₂ Cl ₂ , rt	(—) 62:38	339
Et		Cu-bronze-bentonite, CH ₂ Cl ₂ , rt	(—) 78:22	339
Et		[(Cp)Fe(CO) ₂ (THF)] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , 40°	(0) —	322
Et		OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(1) —	338
Et		[Cu(MeCN) ₄] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , rt, 10 min	(30) 85:15	317
Et		Pd(OAc) ₂ , neat, rt, 10 h	(21) —	77
Et		Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(75) 77:23	51
Et		Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(32) 69:31	51
Et		ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(79) 78:22	51
Et		Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(89) <i>exo</i>	78
Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(79) <i>exo</i>	78
Et		Rh ₂ (O ₂ CC ₃ H _{7-<i>n</i>}) ₄ , CH ₂ Cl ₂ , rt, 5 h	(77) <i>exo</i>	78
Et		Rh ₂ (NHCOF ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(74) <i>exo</i>	78
Et		Rh ₂ (OSCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(75) <i>exo</i>	78
Et		Rh ₂ (O ₂ CCF ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(67) <i>exo</i>	78
Et		Rh ₂ (O ₂ CC ₃ F _{7-<i>n</i>}) ₄ , CH ₂ Cl ₂ , rt, 5 h	(66) <i>exo</i>	78
Et		Iodorrhodium(III)- <i>meso</i> -tetra-(2,4,6-Me ₃ C ₆ H ₂)porphyrin, neat, 60°	(92) 45:55	99
Et		Rh ₂ (OPiv) ₄ , neat, 60°	(98) 72:28	99
Et		Rh ₂ (O ₂ CCPh ₃) ₄ , neat, 60°	(96) 74:26	99
Et		Rh ₂ (O ₂ C-dehydroabietyl) ₄ , neat, 60°	(96) 74:26	99
Et		Rh ₂ (O ₂ C-adamantyl-1) ₄ , neat, 60°	(97) 68:32	99
Et		Rh ₂ (O ₂ C-anthracenyl-9) ₄ , neat, 60°	(93) 64:36	99
Et		Rh ₂ (O ₂ C-mesityl) ₄ , neat, 60°	(97) 59:41	99
Et		Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(89) <i>exo</i>	78
Et		CuOTf, DCE, rt	(37) 84:16	326
Et		4 , DCE, rt	(61) 97:3	326
Et		5 , DCE, rt	(49) 98:2	326
Et		6 , DCE, rt	(31) 99:1	326
Et		7a , neat, 60°	(78) 33:67	99
Et		7b , neat, 60°	(0) —	99
Et		7c , neat, 60°	(80) 28:72	99
Et		7d , neat, 60°	(0) —	99
Et		7e , neat, 60°	(68) 26:74	99
Et		7f , neat, 60°	(0) —	99
Et		7g , neat, 60°	(—) 70:30	99
Et		7h , neat, 60°	(71) 27:73	99
Et		7i , neat, 60°	(77) 42:58	99
Et		7j , neat, 60°	(52) 28:72	99
Et		23b , neat, 60°, 4 h	(22) 74:26	340
Et		24b , neat, 60°, 4 h	(5) 78:22	340
CH ₂ CH ₂ Cl		CuSO ₄ , neat, 90°	(80) —	341
CH ₂ CH ₂ Br		Rh ₂ (OAc) ₄ , 60°	(65) —	342
C ₆ <i>n</i> -Bu		Rh ₂ (OAc) ₄ , neat, rt, 10 h	(80) —	77
<i>n</i> -Bu		Cu(OTf) ₂ , neat, rt, 10 h	(64) —	77

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)


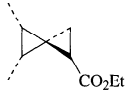

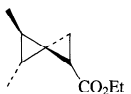
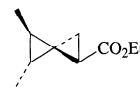

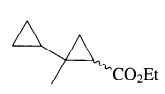
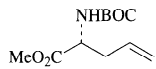
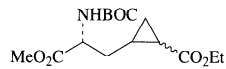

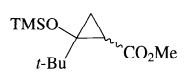

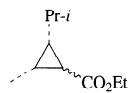

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>t</i> -Bu		Rh ₂ (OAc) ₄ , neat, rt	(89) —	80
<i>t</i> -Bu		Pd(OAc) ₂ , neat, rt	(19) —	80
C ₁₀	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , rt	(62-99) 90:10	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (O ₂ CC ₃ F ₇ - <i>n</i>) ₄ , rt	(62-99) 80:20	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (NHCOCH ₃) ₄ , rt	(62-99) 92:8	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(90) <i>exo</i>	78
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(92) <i>exo</i>	78
C ₁₃	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(96) <i>exo</i>	78
	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(92) <i>exo</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(91) <i>exo</i>	78
	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(92) <i>exo</i>	78
C ₄	R = Et 	CuSO ₄ and Cu-bronze, octane, reflux, 4 h	 (—)	343
	R = Et 	CuSO ₄ and Cu-bronze, octane, reflux, 4 h	 I +  II (—) I:II = 75:25	343
	R = Et 	Cu(acac) ₂ , benzene, reflux	 (79)	41, 344
	R = Et 	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 10 h	 (85) (92) <i>trans:cis</i> = 64:36	195, 345 346
C ₃	R = Me 	Cu(acac) ₂ , benzene, 90°	 (87)	312
C ₄	R = Et 	Iodorhodium(III)- <i>meso</i> -tetraphenylporphyrin, neat, 60° Iodorhodium(III)- <i>meso</i> -tetramesitylporphyrin, DCE, 60°	 (60) <i>trans:cis</i> = 17:83 (82) <i>trans:cis</i> = 13:87	102, 101 101

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
	R		<i>trans:cis</i>		
C ₃	Me	Rh ₂ (OAc) ₄ , neat, rt	(86)	—	80
	Me	Cu(OTf) ₂ , neat, rt	(36)	—	80
	Me	Pd(OAc) ₂ , neat, rt	(30)	—	80
	Me	[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , rt	(67)	67:33	308
C ₄	Et	Rh ₂ (O ₂ CH) ₄ , 40°	(95)	54:46	325
	Et	Rh ₂ (OAc) ₄ , rt	(86)	60:40	325
	Et	Rh ₂ (OAc) ₄ , neat, rt	(95)	60:40	71
	Et	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , rt	(96)	57:43	325
	Et	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 40°	(98)	57:43	325
	Et	Rh ₂ (O ₂ CC ₁₇ H ₃₅ - <i>n</i>) ₄ , rt	(96)	60:40	325
	Et	Rh ₂ (O ₂ CPh) ₄ , 40°	(95)	57:43	325
	Et	Rh ₂ (O ₂ C(CH ₂) ₂ Ph) ₄ , rt	(95)	56:44	325
	Et	Rh ₂ (O ₂ CCH ₂ CPh ₃) ₄ , rt	(98)	49:51	325
	Et	Rh ₂ [O ₂ CC ₆ H ₄ OH-2] ₄ , 40°	(93)	52:48	325
	Et	Rh ₂ [O ₂ CC ₆ H ₄ Bz-2] ₄ , rt	(97)	45:55	325
	Et	Rh ₂ [O ₂ C-2,4-Cl ₂ C ₆ H(NO ₂) ₂ -3,5] ₄ , 40°	(55)	50:50	325
	Et	Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -2) ₄ , rt	(100)	52:48	325
	Et	Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -3) ₄ , rt	(100)	57:43	325
	Et	Rh ₂ (O ₂ CC ₆ I ₂ Me ₃ -2,4,6) ₄ , 40°	(95)	55:45	325
	Et	Rh ₂ (O ₂ CC ₂ H ₄ COMe) ₄ , rt	(93)	55:45	325
	Et	Rh ₂ (O ₂ CCOPh) ₄ , 40°	(87)	57:43	325
	Et	Rh ₂ (O ₂ CCF ₃) ₄ , rt	(69)	58:42	325
	Et	CuSO ₄ , 100°	(50)	—	347
	Et	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(1)	—	91
Et	OsCl ₂ (PPh ₃) ₃ , neat, 50°, 4 h	(1)	—	338	
	Et	Rh ₂ (OAc) ₄ , rt	(60-93)	58:42	323
	Et	Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(60-93)	55:45	323
	Et	Rh ₂ (NHCOCH ₃) ₄ , rt	(60-93)	63:37	323
	Et	Iodorhodium(III)- <i>meso</i> -tetraphenylporphyrin, DCE, 60°	(68)	58:42	101
	Et	Iodorhodium(III)- <i>meso</i> -tetramesitylporphyrin, DCE, 60°	(85)	53:47	101
	Et	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(60)	<i>trans</i>	78
	Et	Rh ₂ (<i>acac</i>) ₄ , CH ₂ Cl ₂ , rt, 5 h	(63)	<i>trans</i>	78
	Et	Iodorhodium(III)- <i>meso</i> -tetra(2,4,6-Me ₃ C ₆ H ₂)porphyrin, neat, 60°	(85)	53:47	99
	Et	Hydridotris(3,5-Me ₂ -1-pyrazolyl)borateCu(C ₂ H ₄), DCE, rt	(63)	50:50	348
	Et	Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(87)	58:42	51
	Et	Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(23)	64:36	51
	Et	ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(92)	58:42	51
	Et	RuCl ₂ (PPh ₃) ₃ , neat, 50°, 4 h	(6)	60:40	52, 338
	Et	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 50°, 4 h	(9)	62:38	52
	Et	RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 50°, 4 h	(6)	68:32	52
	Et	Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 50°, 4 h	(6)	65:35	52
	Et	7a , neat, 60°	(59)	37:63	99
	Et	7c , neat, 60°	(83)	34:66	99
	Et	7e , neat, 60°	(89)	33:67	99
	CH ₂ CN	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	(85)	—	349
	CH ₂ CH ₂ Br	Rh ₂ (OAc) ₄ , 60°	(55)	—	342
C ₁₀	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , rt	(62-99)	71:29	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (O ₂ CC ₃ F ₇ - <i>n</i>) ₄ , rt	(62-99)	58:42	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (NHCOCH ₃) ₄ , rt	(62-99)	78:22	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(71)	<i>trans</i>	78
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(81)	<i>trans</i>	78

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C ₁₂	<i>d</i> -menthyl	Rh ₂ (OAc) ₄ , neat, rt	(95)	60:40	309
C ₁₅	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(74)	<i>trans</i>	78
	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(83)	<i>trans</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(75)	<i>trans</i>	78
	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(93)	<i>trans</i>	78

R	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
			Yield (%)	Diastereomeric Ratio	
C ₃		Rh ₂ (OAc) ₄ , neat, rt	(56)		80, 77
			(68)		77
C ₄	Et	Cu(OTf) ₂ , neat, rt	(15)		80, 77
		Pd(OAc) ₂ , neat, rt	(15)		80, 77
C ₆	<i>n</i> -Bu	MeReO ₃ , neat	(63)		319
		Rh ₂ (OAc) ₄ , neat, rt	(98)		80, 77
	<i>n</i> -Bu	Rh ₂ (OPiv) ₄ , neat, rt, 10 h	(100)		77


R	Substrate	Conditions	<i>trans:cis</i>		Refs.	
			Yield (%)	Diastereomeric Ratio		
C ₄		Rh ₂ (OAc) ₄ , rt	(60-93)	74:26	323	
			Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(60-93)	60:40	323
			Rh ₂ (NHCOCH ₃) ₄ , rt	(60-93)	83:17	323
			Rh ₂ (OAc) ₄ , neat, rt	(87)	81:19	71
			Rh ₆ (CO) ₁₆ , neat, rt	(42)	82:18	71
			CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(23)	88:12	71
			Cu(OTf) ₂ , neat, rt	(54)	85:15	71
			Cu/bronze, neat, rt	(5)	89:11	71
			Cu(acac) ₂ , neat, 60°	(20)	91:9	71
			PdCl ₂ •2PhCN, neat, rt	(34)	71:29	71
			Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(75)	<i>trans</i>	78
			Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(83)	<i>trans</i>	78
			Rh ₂ (OAc) ₄ , rt	(62-99)	86:14	323
			Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(62-99)	64:36	323
Rh ₂ (NHCOCH ₃) ₄ , rt	(62-99)	89:11	323			
C ₁₀	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(84)	<i>trans</i>	78	
		Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(89)	<i>trans</i>	78	
C ₁₂	<i>d</i> -menthyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	(87)	81:19	309	
C ₁₃	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(89)	<i>trans</i>	78	
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(93)	<i>trans</i>	78	
		Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(99)	<i>trans</i>	78	

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ R = Et		Iron <i>meso</i> -tetra-(pentafluorophenyl)-porphyrin chloride, CH ₂ Cl ₂ , rt, 2 h	 (—)	57
C ₃ R		Rh ₂ (OAc) ₄ , neat, rt, 10 h	 (70)	77
Me		Rh ₂ (OPiv) ₄ , neat, rt, 10 h	(75)	77
Me		Cu(OTf) ₂ , neat, rt, 10 h	(30)	77
Me		Pd(OAc) ₂ , neat, rt, 10 h	(<8)	77
Me		[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , rt	(47)	308
Me		Ru ₂ (CO) ₄ (μ-OAc) ₂ (MeCN) ₂ , CH ₂ Cl ₂ , 60°	(12)	308
C ₄ Et		MeReO ₃ , neat	(57)	319
CH ₂ CN		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	(80)	349
(CH ₂) ₂ Br		Rh ₂ (OAc) ₄ , 60°	(65)	342
C ₆ (CH ₂) ₂ NMe ₂		Cu/CuSO ₄ , neat, 110°	(40)	350
C ₈ (CH ₂) ₂ NEt ₂		Cu/CuSO ₄ , neat, 110°	(40)	350
C ₄ R = Et		Cu-bronze, neat, reflux, 19 h	 (73)	320
R = Et		Rh ₂ (OAc) ₄ , neat, rt	 <i>trans:cis</i> (84) 63:37	71
		Rh ₆ (CO) ₁₆ , neat, rt	(69) 64:36	71
		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(51) 67:33	71
		PdCl ₂ •2PhCN, neat, rt	(34) 62:38	71
		Rh ₆ (CO) ₁₆ , neat, rt	(69) —	318
		PdCl ₂ •PhCN, neat, rt	(34) —	318
		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(51) —	318
		Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(93) 64:36	51
		Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(46) 65:35	51
		ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(91) 62:38	51
		(7PPH ₂ -8-H-7,8-C ₂ B ₉ H ₁₀) Rh(PPh ₃) ₂ , neat, 4 h, 80°	(88) 59:41	351
R = Et		Cu, 95°, 1 h	 (85)	352
R = Et		Cu-bronze, methylcyclohexane, reflux, 4 h	 (—)	329
C ₃ R		CuSO ₄ , DME, 110°	(—)	353
Me		Rh ₂ (OAc) ₄ , neat, rt	(88)	80
C ₄ Et		Cu(OTf) ₂ , neat, rt	(47)	80
Et		Pd(OAc) ₂ , neat, rt	(95)	80
Et		Zeolite NaCuX-57	(75)	336

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)


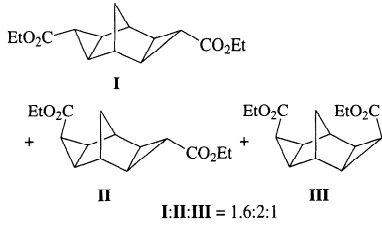


Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
R = Et		(π -allyl)PdCl, neat, 0°, 5 h, 2 eq EDA	 I II III I:II:III = 1.6:2:1		354
R			 <i>exo:endo</i>		
Et		Cu(OTf) ₂	(—)	30:70	355
Et		Rh(II), rt, 12 h	(95)	—	356
Et		Iodorrhodium(III)- <i>meso</i> -tetraphenylporphyrin, neat, 60°	(71)	35:65	102
Et		Rh ₂ (OAc) ₄ , π	(60-93)	67:33	323
Et		Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(60-93)	60:40	323
Et		Rh ₂ (NHCOCH ₃) ₄ , rt	(60-93)	78:22	323
Et		Rh ₂ (OAc) ₄ , neat, rt	(95)	—	80
Et		Cu(OTf) ₂ , neat, rt	(95)	—	80
Et		Pd(OAc) ₂ , neat, π	(87)	—	80
Et		Iodorrhodium(III)- <i>meso</i> -tetraphenylporphyrin, DCE, 60°	(71)	—	101
Et		Iodorrhodium(III)- <i>meso</i> -tetramesitylporphyrin, DCE, 60°	(76)	—	101
Et		Iodorrhodium(III)- <i>meso</i> -cyanoctaethylporphyrin, DCE, 60°	(67)	—	101
Et		Iodorrhodium(III)- <i>meso</i> -tetra- <i>o</i> -tolylporphyrin, DCE, 60°	(74)	—	101
Et		Zeolite NaCuX-57	(78)	—	336
Et		(7PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)/Rh(PPh ₃) ₂ , neat, 4 h, 80°	(9)	59:41	351
Et		RuCl(<i>p</i> -cymene)(TsNC ₆ H ₄ NH ₂) ₄ , neat, 80°	(0)	—	357
Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(67)	<i>exo</i>	78
Et		Rh ₂ (acac) ₄ , CH ₂ Cl ₂ , rt, 5 h	(82)	<i>exo</i>	78
Et		Iodorrhodium(III)- <i>meso</i> -tetra-(2,4,6-Me ₃ C ₆ H ₂)porphyrin, neat, 60°	(76)	32:68	99
Et		7a , neat, 60°	(39)	31:69	99
Et		7c , neat, 60°	(9)	45:55	99
Et		23b , neat, 60°, 4 h	(0)	—	340
Et		24b , neat, 60°, 4 h	(0)	—	340
C ₁₀	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , π	(62-99)	76:24	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(62-99)	83:17	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (NHCOCH ₃) ₄ , rt	(62-99)	67:33	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(76)	<i>exo</i>	78
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(83)	<i>exo</i>	78
C ₁₃	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(86)	<i>exo</i>	78
	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(82)	<i>exo</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(95)	<i>exo</i>	78
	2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(92)	<i>exo</i>	78

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ R = Me		CuSO ₄ , 90°	 (60)	358
R = Me		CuSO ₄ , 90°	 (---)	358
R = Me		CuSO ₄ , 90°	 (---)	358
R = Me		Cu(acac) ₂ , benzene, heat	 (58)	312
		Temp 90° 100°	(75) <i>trans:cis</i> = 74:26	294
R = Me		Cu(acac) ₂ , solvent, reflux	 (76) <i>trans:cis</i> = 53:47	294, 312
		Solvent benzene ethyl acetate	(77) <i>trans:cis</i> = 53:47	194
R = Me		Cu(acac) ₂ , ethyl acetate, reflux	 (74)	294
R = Me		Cu(acac) ₂ , ethyl acetate, reflux	 (62) <i>trans:cis</i> = 60:40	294
C ₄ R = Et		Cu/bronze, neat, 135°	 (95) <i>exo:endo</i> = 67:33	359
R			<i>exo:endo</i>	
Et		Rh ₂ (O ₂ CH) ₄ , 60°	(---) 66:34	325
Et		Rh ₂ (OAc) ₄ , 60°	(---) 69:31	325
Et		Rh ₂ (O ₂ CBu- <i>n</i>) ₄ , 60°	(---) 69:31	325
Et		Rh ₂ (OAc) ₄ , neat, rt	(75) —	80
Et		Cu(OTf) ₂ , neat, rt	(30) —	80
Et		Pd(OAc) ₂ , neat, rt	(40) —	80
Et		Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(89) 67:33	51
Et		Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(26) 63:37	51
Et		ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(88) 67:33	51
R = Et		CuCl•PMe ₃ , neat, reflux	 (40)	337
		Rh ₂ (OAc) ₄ , neat, rt	(80) <i>trans:cis</i> = 73:27	71

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<u>R</u>			<u>trans:cis</u>	
Et		Rh ₂ (OAc) ₄ , neat, rt	(78) 71:29	71
Et		Rh ₂ (OAc) ₄ , Et ₂ O, rt	(80) 71:29	94
Et		MeReO ₃ , neat	(74) —	319
Et		Rh ₆ (CO) ₁₆ , neat, rt	(59) 72:28	71, 318
Et		PdCl ₂ •PhCN, neat, rt	(39) 60:40	71, 318
Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(54) 81:19	71, 318
Et		CuCl•P(OPh) ₃ , neat, rt	(35) 82:18	71
Et		Cu(acac) ₂ , neat, 60°	(44) 83:17	71
C ₃	R = Me 	Cu(acac) ₂	(54)	360
C ₄	R = Et 			318
		Rh ₆ (CO) ₁₆ , neat, rt	(70)	
		PdCl ₂ •PhCN, neat, rt	(33)	
		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(42)	
	R = Et 	Cu(F ₃ CCOCHCOCF ₃) ₂ , benzene, reflux, 3 h	(57)	361
<u>R</u>			<u>trans:cis</u>	
Et		Cu, 100°, 1 h	(79) —	352
Et		Rh ₂ (OAc) ₄ , neat, rt	(70) 42:58	71
Et		Rh ₆ (CO) ₁₆ , neat, rt	(83) 42:58	71
Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(7) 55:45	71
Et		PdCl ₂ •2PhCN, neat, rt	(28) 38:62	71
C ₃	R = Me 	Cu(acac) ₂ , 100°, 3 h	(79)	307
C ₄	R = Et 	CuSO ₄ , cyclohexane, reflux	(30) <i>trans:cis</i> = 75:25	345
	R = Et 	Cu(acac) ₂ , benzene, reflux	(72)	362
	R = Et 	Pd(OAc) ₂ , neat, rt	(73)	80
<u>R</u>	<u>R¹</u>		<u>trans:cis</u>	
Et	Me	CuSO ₄ , benzene, 75°	(23) —	363
Et	Me	Rh ₂ (OAc) ₄ , neat, rt	(60) 67:33	71
Et	<i>t</i> -Bu	CuSO ₄ , benzene, 75°	(51) —	363

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
	<u>R</u>		<u>trans:cis</u>		
C ₃	Me	Cu(acac) ₂ , 100°, 3 h	(52)	—	307
	Me	[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , rt	(95)	62:38	308
	Me	Ru ₂ (CO) ₄ (μ-OAc) ₂ (MeCN) ₂ , CH ₂ Cl ₂ , rt	(58)	70:30	308
	Me	Ru ₂ (CO) ₄ (μ-OAc) ₂ (MeCN) ₂ , neat, 60°	(94)	60:40	308
	Me	13a , neat, 60°, 4 h	(66)	65:35	364
	Me	14a , neat, 60°, 4 h	(75)	71:29	364
	Me	14c , neat, 60°, 4 h	(57)	83:17	364
C ₄	Et	14f , neat, 60°, 4 h	(53)	86:14	364
	Et	Rh ₂ (O ₂ CH) ₄ , 60°	(98)	51:49	325
	Et	Rh ₂ (OAc) ₄ , rt	(91)	60:40	325
	Et	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , rt	(99)	62:38	325
	Et	Rh ₂ (O ₂ CC ₁₇ H ₃₅ - <i>n</i>) ₄ , rt	(98)	60:40	325
	Et	Rh ₂ (O ₂ CC ₆ H ₅) ₄ , 60°	(97)	55:45	325
	Et	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 60°	(100)	51:49	325
	Et	Rh ₂ [O ₂ C(CH ₂) ₂ C ₆ H ₅] ₄ , rt	(100)	54:46	325
	Et	Rh ₂ [O ₂ CCH ₂ C(C ₆ H ₅) ₃] ₄ , rt	(100)	45:55	325
	Et	Rh ₂ [O ₂ CC ₆ H ₄ (OH-2)] ₄ , 60°	(91)	46:54	325
	Et	Rh ₂ [O ₂ CC ₆ H ₄ (COPh-2)] ₄ , rt	(98)	46:54	325
	Et	Rh ₂ [O ₂ C-2,4-Cl ₂ C ₆ H(NO ₂) ₂ -3,5] ₄ , rt	(65)	48:52	325
	Et	Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -2) ₄ , rt	(86)	51:49	325
	Et	Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -3) ₄ , rt	(87)	55:45	325
	Et	Rh ₂ (O ₂ CC ₆ H ₂ Me ₃ -2,4,6) ₄ , 60°	(98)	50:50	325
	Et	Rh ₂ [O ₂ CC ₂ H ₄ (COMe)] ₄ , rt	(98)	60:40	325
	Et	Rh ₂ [O ₂ CCOC ₆ H ₅] ₄ , 60°	(89)	51:49	325
	Et	Rh ₂ (O ₂ CCF ₃) ₄ , rt	(99)	53:47	325
	Et	Rh ₂ (OAc) ₄ , rt	(92)	60:40	80
	Et	Rh ₂ (O ₂ CBu- <i>n</i>) ₄ , rt	(60)	60:40	80
	Et	Rh ₂ (O ₂ CC ₆ H ₁₃ - <i>n</i>) ₄ , rt	(95)	57:43	80
	Et	Rh ₂ (O ₂ CCF ₃) ₄ , rt	(66)	47:53	80
	Et	RhCl ₃ •3H ₂ O, rt	(7)	—	80
Et	RhCl(PPh ₃) ₃	(12)	—	80	
Et	Mo ₂ (OAc) ₄ , rt	(5)	—	80	
Et	Ru ₂ (OAc) ₄ Cl, rt	(38)	64:36	80	
Et	PdCl ₂ , rt	(70)	—	80	
Et	Pd(OAc) ₂ , rt	(98)	67:33	80	
Et	PdCl•2PhCN, rt	(65)	70:30	80	
Et	Pd(PPh ₃) ₄ , rt	(57)	69:31	80	
Et	Pd/C, rt	(0)	—	80	
Et	Cu(acac) ₂ , rt	(65)	68:32	80	
Et	Cu(OTf) ₂ , rt	(80)	—	80	
Et	CuCl•P(OPh) ₃ , neat, rt	(84)	71:29	71	
Et	Cu(OTf) ₂ , neat, 60°	(97)	66:34	71	
Et	Cu-bronze, neat, 60°	(53)	66:34	71	
Et	Cu(acac) ₂ , neat, 60°	(71)	72:28	71	
Et	Hydridotris(3,5-dimethyl-1-pyrazolyl)-borateCu(C ₂ H ₄), DCE, rt	(75)	43:57	348, 365	
Et	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(91)	53:47	351	
Et	(7-PPh ₂ -8-Me-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(92)	52:48	351	
Et	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(1,5-cyclooctadiene), neat, 4 h, 100°	(91)	54:46	351	
Et	RuCl ₂ (PPh ₃) ₃ , neat, 20°, 4 h	(37)	67:33	52	
Et	RuCl ₂ (PPh ₃) ₃ , neat, 30°, 4 h	(43)	66:34	338	
Et	RuCl ₂ (PPh ₃) ₃ , neat, 40°, 4 h	(55)	61:39	52	
Et	RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(93)	56:44	52, 338	
Et	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 20°, 4 h	(38)	68:32	52	

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Et		RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 40°, 4 h	(53) 62:38	52
Et		RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(89) 56:44	52
Et		RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 20°, 4 h	(33) 71:29	52
Et		RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 40°, 4 h	(48) 71:29	52
Et		RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(85) 70:30	52
Et		Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 20°, 4 h	(41) 65:35	52
Et		Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 40°, 4 h	(54) 62:38	52
Et		Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(91) 60:40	52
Et		RuCl ₂ (AsPh ₃) ₃ , neat, 60°, 4 h	(92) 58:42	52
Et		RuCl ₂ (SbPh ₃) ₃ , neat, 60°, 4 h	(94) 70:30	52
Et		(5,10,15,20-tetraphenylporphyrinato)Ru-(diethoxycarbonyl)carbene MeOH, CH ₂ Cl ₂ , rt	(85) 93:7	366
Et		(5,10,15,20-tetraphenylporphyrinato)Ru-(diethoxycarbonyl)carbene MeOH, toluene, reflux	(66) —	366
Et		(CO) ₅ WC(OMe)Ph, 35°	(41) 62:38	321
Et		Pd(OAc) ₂ , benzene, 40°	(76) 67:33	79
Et		[(Cp)Fe(CO) ₂ (THF)] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , 40°	(68) 15:85	322
Et		OsCl ₂ (PPh ₃) ₃ , neat, 30°, 4 h	(18) 71:29	338
Et		OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(52) 69:31	338
Et		Rh ₆ (CO) ₁₆ , neat, rt	(87) —	318
Et		[Rh(PE-CO ₂) ₂] ₂ , toluene, 100°	(96) 64:36	367
Et		PdCl ₂ •PhCN, neat, rt	(52) —	318
Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(80) —	318
Et		Rh ₂ (OAc) ₄ , neat, rt	(93) 62:38	71
Et		Rh ₆ (CO) ₁₆ , neat, rt	(86) 63:37	71
Et		CuCl•P(OPr- <i>i</i>) ₃ , neat, rt	(88) 74:26	71
Et		PdCl ₂ •2PhCN, neat, rt	(52) 62:38	71
Et		[Cu(MeCN) ₄] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , rt, 10 min	(60) 62:38	317
Et		[Cu(MeCN) ₂ (PPh ₃) ₂] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , rt, 2 h	(55) 71:29	317
Et		[Cu(MeCN)(PPh ₃) ₃] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , rt, 16 h	(27) 70:30	317
Et		Cu(BF ₄)(PCy ₃) ₂ , CH ₂ Cl ₂ , rt, 4.5 h	(29) 80:20	317
Et		Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(68) <i>trans</i>	78
Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(62) <i>trans</i>	78
Et		Rh ₂ (O ₂ CC ₃ H _{7-<i>n</i>}) ₄ , CH ₂ Cl ₂ , rt, 5 h	(60) <i>trans</i>	78
Et		Rh ₂ (NHCOCF ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(59) <i>trans</i>	78
Et		Rh ₂ (OCSCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(62) <i>trans</i>	78
Et		Rh ₂ (O ₂ CCF ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(56) <i>trans</i>	78
Et		Rh ₂ (O ₂ CC ₃ F _{7-<i>n</i>}) ₄ , CH ₂ Cl ₂ , rt, 5 h	(52) <i>trans</i>	78
Et		Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(68) <i>trans</i>	78
Et		Pt(PPh ₃) ₄ , neat, 60°	(76) 61:39	368
Et		Pt(PPh ₃) ₄ , neat, 100°	(95) 61:39	368
Et		PtCl ₂ , neat, 60°	(48) 62:38	368
Et		PtCl ₂ , neat, 100°	(94) 61:39	368
Et		[PtCl ₂ (cyclohexene)] ₂ , neat, 60°	(49) 61:39	368
Et		[PtCl ₂ (cyclohexene)] ₂ , neat, 100°	(94) 61:39	368
Et		<i>cis</i> -PtCl ₂ (benzonitrile) ₂ , neat, 60°	(47) 61:39	368
Et		<i>cis</i> -PtCl ₂ (benzonitrile) ₂ , neat, 100°	(92) 61:39	368
Et		<i>cis</i> -PtCl ₂ (pyr) ₂ , neat, 60°	(34) 62:38	368
Et		<i>cis</i> -PtCl ₂ (pyr) ₂ , neat, 100°	(88) 61:39	368
Et		<i>cis</i> -PtCl ₂ (PPh ₃) ₂ , neat, 60°	(75) 62:38	368
Et		<i>cis</i> -PtCl ₂ (PPh ₃) ₂ , neat, 100°	(92) 62:38	368
Et		<i>trans</i> -PtCl ₂ (PPh ₃) ₂ , neat, 60°	(69) 61:39	368
Et		<i>trans</i> -PtCl ₂ (PPh ₃) ₂ , neat, 100°	(91) 62:38	368
Et		PtBr ₂ , neat, 60°	(43) 61:39	368
Et		PtBr ₂ , neat, 100°	(89) 61:39	368
Et		PtI ₂ , neat, 60°	(58) 61:39	368
Et		PtI ₂ , neat, 100°	(66) 61:39	368
Et		PtI ₂ (NH ₃) ₂ , neat, 60°	(67) 62:38	368
Et		PtI ₂ (NH ₃) ₂ , neat, 100°	(91) 61:39	368

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Et		PtCl ₄ , neat, 60°	(79) 58:42	368
Et		PtCl ₄ , neat, 100°	(85) 54:46	368
Et		PtBr ₄ , neat, 60°	(54) 62:38	368
Et		PtBr ₄ , neat, 100°	(92) 61:39	368
Et		Pt(C ₂ H ₄)(PPh ₃) ₂ , CH ₂ Cl ₂ , rt, 24 h	(—) —	369
Et		Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(86) 59:41	51
Et		Cl(Ph ₃ P) ₂ Ru(Me ₇ C ₂ B ₉ H ₁₀), neat, 60°	(81) 55:45	51
Et		ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₇), neat, 60°	(93) 58:42	51
Et		[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 60°	(74) 61:39	81
Et		[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(97) 61:39	81
Et		[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 60°	(78) 62:38	81
Et		[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(96) 61:39	81
Et		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂], neat, 60°	(78) 64:36	357
Et		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂], neat, 100°	(89) 63:37	357
Et		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂], neat, 60°	(94) 63:37	357
Et		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂], neat, 100°	(81) 60:40	357
Et		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂], neat, 60°	(80) 62:38	357
Et		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂], neat, 100°	(90) 62:38	357
Et		RuCl(<i>p</i> -cymene)[TsN-2-H ₂ NC ₆ H ₄], neat, 60°	(75) 62:38	357
Et		RuCl(<i>p</i> -cymene)[TsN-2-H ₂ NC ₆ H ₄], neat, 100°	(87) 61:39	357
Et		RuCl(<i>p</i> -cymene)(2-TsNpyridine), neat, 60°	(65) 62:38	357
Et		RuCl(<i>p</i> -cymene)(2-TsNpyridine), neat, 100°	(85) 65:35	357
Et		RuCl(<i>p</i> -cymene)[2-(TsNCH ₂)pyridine], neat, 60°	(77) 65:35	357
Et		RuCl(<i>p</i> -cymene)[2-(TsNCH ₂)pyridine], neat, 100°	(86) 65:35	357
Et		Cu/bronze-K10 montmorillonite, CH ₂ Cl ₂ , rt	(—) 44:56	339
Et		Cu/bronze-bentonite, CH ₂ Cl ₂ , rt	(—) 64:36	339
Et		Cu/bronze-laponite, CH ₂ Cl ₂ , rt	(—) 58:42	339
Et		Iron <i>meso</i> -tetra- <i>p</i> -tolylporphyrin, CH ₂ Cl ₂ , rt, 1 h	(—) 90:10	57
Et		Iron <i>meso</i> -tetra- <i>p</i> -tolylporphyrin chloride, CH ₂ Cl ₂ , 40°, 10 h	(—) 85:15	57
Et		Iron <i>meso</i> -tetra- <i>p</i> -tolylporphyrin chloride/cobaltocene, CH ₂ Cl ₂ , rt, 2 h	(—) 90:10	57
Et		Iron <i>meso</i> -tetra- <i>p</i> -MeOphenylporphyrin chloride/cobaltocene, CH ₂ Cl ₂ , rt, 3 h	(—) 90:10	57
Et		Iron <i>meso</i> -tetra(pentafluorophenyl)porphyrin chloride, CH ₂ Cl ₂ , rt, 6 h	(—) 86:14	57
Et		Iron <i>meso</i> -tetramesitylporphyrin chloride/cobaltocene, CH ₂ Cl ₂ , rt, 2 h	(—) 93:7	57
Et		Iron octaethylporphyrin chloride/ cobaltocene, CH ₂ Cl ₂ , rt, 4 h	(—) 91:9	57
Et		Osmium <i>meso</i> -tetra- <i>p</i> -tolylporphyrin- (CO)(pyr), toluene, rt, 2 h	(44) 90:10	90
Et		Osmium <i>meso</i> -tetra- <i>p</i> -tolylporphyrin dimer, toluene, rt, 2 h	(79) 91:9	90
Et		Ru(<i>meso</i> -tetraphenylporphyrin)(CO), neat, rt, 4 h	(—) 93:7	84
Et		Ru(<i>meso</i> -tetramesitylporphyrin)(CO), neat, rt, 4 h	(—) 89:11	84
Et		Ru(<i>meso</i> -tetramesitylporphyrin)(O) ₂ , neat, rt, 4 h	(—) 88:12	84
Et		[Ru(<i>meso</i> -tetraphenylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(45) 90:10	370
Et		[Ru(<i>meso</i> -tetramesitylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(68) 89:11	370
Et		[Ru(octaethylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(25) 92:8	370

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Et		[Ru(tetrapropylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(39) 92:8	370
Et		CuOTf, DCE, rt	(70) 59:41	326
Et		1, DCE, 60°, 4 h	(79) 73:27	371
Et		2, DCE, 60°, 4 h	(89) 73:27	371
Et		3, DCE, 60°, 4 h	(78) 72:28	371
Et		4, DCE, rt	(83) 86:14	326
Et		5, DCE, rt	(70) 85:15	326
Et		6, DCE, rt	(66) 82:18	326
Et		8a, neat, 80°, 4 h	(71) 75:25	372
Et		8b, neat, 80°, 4 h	(69) 75:25	372
Et		9, neat, 80°, 4 h	(91) 76:24	372
Et		10a, neat, 80°, 4 h	(26) 76:24	372
Et		10b, neat, 60°, 4 h	(38) 82:18	372
Et		10b, neat, 80°, 4 h	(52) 82:18	372
Et		11a, neat, 80°, 4 h	(44) 76:24	372
Et		11b, neat, 60°, 4 h	(34) 67:33	372
Et		11b, neat, 60°, 13 h	(44) 73:27	372
Et		11b, neat, 80°, 4 h	(54) 75:25	372
Et		11b, neat, 80°, 8 h	(56) 75:25	372
Et		11b, neat, 100°, 2 h	(58) 78:22	372
Et		11b, neat, 100°, 4 h	(59) 77:23	372
Et		12, CH ₂ Cl ₂ , 60°	(54) 89:11	106
Et		13a, neat, 60°, 4 h	(70) 72:28	364
Et		13a, neat, 100°, 4 h	(72) 82:18	364
Et		13b, neat, 60°, 4 h	(62) 66:34	364
Et		13b, neat, 100°, 4 h	(—) —	364
Et		13c, neat, 60°, 4 h	(75) 65:35	364
Et		13c, neat, 100°, 4 h	(96) 71:29	364
Et		13d, neat, 60°, 4 h	(73) 64:36	364
Et		13d, neat, 100°, 4 h	(94) 76:24	364
Et		13e, neat, 60°, 4 h	(57) 66:34	364
Et		13e, neat, 100°, 4 h	(90) 79:21	364
Et		13f, neat, 60°, 4 h	(71) 69:31	364
Et		13f, neat, 100°, 4 h	(84) 79:21	364
Et		14a, neat, 60°, 4 h	(69) 72:28	364
Et		14a, neat, 100°, 4 h	(57) 83:17	364
Et		14b, neat, 60°, 4 h	(57) 83:17	364
Et		14b, neat, 100°, 4 h	(72) 75:25	364
Et		14c, neat, 60°, 4 h	(60) 84:16	364
Et		14c, neat, 100°, 4 h	(84) 71:29	364
Et		14d, neat, 60°, 4 h	(57) 84:16	364
Et		14d, neat, 100°, 4 h	(71) 82:18	364
Et		14e, neat, 60°, 4 h	(63) 88:12	364
Et		14e, neat, 100°, 4 h	(66) 85:15	364
Et		14f, neat, 60°, 4 h	(56) 87:13	364
Et		14f, neat, 100°, 4 h	(73) 76:24	364
Et		15, neat, 60°, 4 h	(93) 62:38	364
Et		15, neat, 100°, 4 h	(93) 61:39	364
Et		16, neat, 60°, 4 h	(78) 81:19	364
Et		16, neat, 100°, 4 h	(77) 75:25	364
Et		17, neat, 60°, 4 h	(52) 61:39	364
Et		17, neat, 100°, 4 h	(91) 61:39	364
Et		18, neat, 60°, 4 h	(83) 68:32	364
Et		18, neat, 100°, 4 h	(60) 79:21	364
Et		19, neat, 60°, 4 h	(42) 66:34	364
Et		19, neat, 100°, 4 h	(68) 78:22	364
Et		20, CH ₂ Cl ₂ , rt, 24 h	(60) 64:36	364
Et		21, CH ₂ Cl ₂ , rt, 24 h	(52) 65:35	364
Et		22, CH ₂ Cl ₂ , rt, 24 h	(55) 65:35	364

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Et		23a , neat, rt, 4 h	(23) 61:39	340
Et		23a , neat, 40°, 4 h	(51) 59:41	340
Et		23a , neat, 60°, 4 h	(71) 57:43	340
Et		23b , neat, rt, 4 h	(25) 62:38	340
Et		23b , neat, 40°, 4 h	(50) 57:43	340
Et		23b , neat, 60°, 4 h	(71) 55:45	340
Et		24a , neat, rt, 4 h	(19) 63:37	340
Et		24a , neat, 40°, 4 h	(45) 63:37	340
Et		24a , neat, 60°, 4 h	(68) 62:38	340
Et		24b , neat, rt, 4 h	(12) 63:37	340
Et		24b , neat, 40°, 4 h	(43) 62:38	340
Et		24b , neat, 60°, 4 h	(66) 62:38	340
Et		25g , CH ₂ Cl ₂ , rt, 3 h	(47) 85:15	373
Et		27 , CH ₂ Cl ₂ , rt, 3 h	(66) 70:30	373
Et		McRcO ₃ , neat	(81) —	319
Et		Iodorrhodium(III) <i>meso</i> -tetraphenylporphyrin, neat, 60°	(71) 47:53	102
Et		Rh ₂ (OAc) ₄ , rt	(95) 62:38	323
Et		Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(81) 52:48	323
Et		Rh ₂ (NHCOCH ₃) ₄ , rt	(89) 68:32	323
Et		Iodorrhodium(III) <i>meso</i> -tetraphenylporphyrin, DCE, 60°	(71) 53:47	101
Et		Iodorrhodium(III) <i>meso</i> -tetramesitylporphyrin, DCE, 60°	(78) 51:49	101
Et		Iodorrhodium(III) <i>meso</i> -tetra(<i>p</i> -tolyl)porphyrin, 0°	(68) —	374
Et		[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(59) 64:36	91
Et		[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(78) 63:37	91
	NMe ₂	Rh ₂ (OAc) ₄ , rt	(74) 69:31	323
	NMe ₂	Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(67) 60:40	323
	NMe ₂	Rh ₂ (NHCOCH ₃) ₄ , rt	(70) 71:29	323
C ₆	<i>t</i> -Bu	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	(68) 66:34	309
	<i>t</i> -Bu	13a , neat, 60°, 4 h	(66) 72:28	364
	<i>t</i> -Bu	14a , neat, 60°, 4 h	(65) 86:14	364
	<i>t</i> -Bu	14c , neat, 60°, 4 h	(60) 94:6	364
	<i>t</i> -Bu	14f , neat, 60°, 4 h	(58) 95:5	364
C ₈	N(<i>Pr</i> - <i>i</i>) ₂	Rh ₂ (OAc) ₄ , rt	(53) 98:2	323
	N(<i>Pr</i> - <i>i</i>) ₂	Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(51) 92:8	323
	N(<i>Pr</i> - <i>i</i>) ₂	Rh ₂ (NHCOCH ₃) ₄ , rt	(47) 99:1	323
C ₁₀	CMe(<i>Pr</i> - <i>i</i>) ₂	Rh ₂ (OAc) ₄ , rt	(95) 71:29	323
	CMe(<i>Pr</i> - <i>i</i>) ₂	Rh ₂ (O ₂ CC ₃ F ₇) ₄ , rt	(83) 52:48	323
	CMe(<i>Pr</i> - <i>i</i>) ₂	Rh ₂ (NHCOCH ₃) ₄ , rt	(87) 82:18	323
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(71) <i>trans</i>	78
	2,3,4-Me ₃ -3-pentyl	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(87) <i>trans</i>	78
C ₁₃	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(73) <i>trans</i>	78
	3- <i>i</i> -Pr-2-Me-3-heptyl	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(93) <i>trans</i>	78
C ₁₇	2,6-(<i>t</i> -Bu) ₂ -4-MePh	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 5 h	(84) <i>trans</i>	78
	2,6-(<i>t</i> -Bu) ₂ -4-MePh	Rh ₂ (NHCOCH ₃) ₄ , CH ₂ Cl ₂ , rt, 5 h	(98) <i>trans</i>	78

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor		Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
	<u>R</u>	<u>R¹</u>		<u>trans:cis</u>		
C ₃	Me	OCHF ₂	Cu/CuSO ₄ , TCE, 100°	(42)	50:50	375
	Me	OAc	Cu/CuSO ₄ , TCE, 100°	(60)	50:50	375
C ₄	Et	Cl	Rh ₂ (O ₂ CH) ₄ , 60°	(—)	55:45	325
	Et	Cl	Rh ₂ (OAc) ₄ , 60°	(—)	61:39	325
	Et	Cl	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 60°	(—)	62:38	325
	Et	Cl	Pd(OAc) ₂	(—)	—	376
	Et	Cl	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(57)	65:35	91
	Et	Cl	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(75)	66:34	91
	Et	Cl	Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(91)	55:45	51
	Et	Cl	Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(73)	56:44	51
	Et	Cl	ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₇), neat, 60°	(96)	56:44	51
	Et	Cl	Pd(OAc) ₂ , neat, rt	(86)	—	80
	Et	Cl	RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(89)	64:36	52, 338
	Et	Cl	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(87)	71:29	52
	Et	Cl	RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(81)	71:29	52
	Et	Cl	Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(83)	71:29	52
	Et	Cl	OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(47)	70:30	338
	Et	Cl	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(89)	66:34	351
	Et	Cl	(7-PPh ₂ -8-Me-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(92)	63:37	351
	Et	Cl	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)-Rh(1,5-cyclooctadiene), neat, 4 h, 100°	(87)	66:34	351
	Et	Cl	[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(94)	67:33	81
	Et	Cl	[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(93)	68:32	81
	Et	Cl	RuCl(<i>p</i> -cymene)(TsNC ₆ H ₄ NH ₂ -2), neat, 80°	(85)	71:29	357
	Et	Cl	Hydridotris(3,5-dimethyl-1-pyrazolyl)borateCu(C ₂ H ₄), DCE, rt	(—)	58:42	365
	Et	Cl	[Ru(<i>meso</i> -tetraphenylporphyrin)(CO)], neat, rt, 4 h	(—)	93:7	84
	Et	Cl	[Ru(<i>meso</i> -tetramesitylporphyrin)(CO)], neat, rt, 4 h	(—)	89:11	84
	Et	Cl	[Ru(<i>meso</i> -tetraphenylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(44)	93:7	370
	Et	Cl	[Ru(<i>meso</i> -tetramesitylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(53)	91:9	370
	Et	Cl	[Ru(octaethylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(23)	92:8	370
	Et	Cl	[Ru(tetrapropylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(21)	93:7	370
	Et	Cl	13a , neat, 60°, 4 h	(75)	76:24	364
	Et	Cl	13d , neat, 60°, 4 h	(71)	69:31	364
	Et	Cl	14a , neat, 60°, 4 h	(76)	82:18	364
	Et	Cl	14d , neat, 60°, 4 h	(63)	87:13	364
	Et	Cl	14f , neat, 60°, 4 h	(60)	87:13	364
	Et	Cl	23b , neat, 60°, 4 h	(72)	69:31	340
	Et	Cl	24b , neat, 60°, 4 h	(67)	70:30	340
	Et	F	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(93)	62:38	351
	Et	F	Pd(OAc) ₂	(—)	—	376
	Et	Br	Pd(OAc) ₂	(—)	—	376

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
Et	Br	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(90)	68:32	351
Et	Br	RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(85)	68:32	52
Et	Br	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(84)	61:39	52
Et	Br	RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(80)	68:32	52
Et	Br	Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(80)	62:38	52
Et	NO ₂	Hydridotris(3,5-dimethyl-1-pyrazolyl)- borateCu(C ₂ H ₄), DCE, rt	(—)	—	365
Et	NO ₂	Pd(OAc) ₂	(—)	—	52
Et	CN	Pd(OAc) ₂	(—)	—	52
Et	CF ₃	Hydridotris(3,5-dimethyl-1-pyrazolyl)- borateCu(C ₂ H ₄), DCE, rt	(—)	50:50	365
Et	Me	Rh ₂ (O ₂ CH) ₄ , 60°	(—)	55:45	325
Et	Me	Rh ₂ (OAc) ₄ , 60°	(—)	60:40	325
Et	Me	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 60°	(—)	60:40	325
Et	Me	Pd(OAc) ₂	(—)	—	376
Et	Me	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(66)	67:33	91
Et	Me	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(85)	61:39	91
Et	Me	Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(89)	60:40	51
Et	Me	Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(77)	60:40	51
Et	Me	ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(93)	63:37	51
Et	Me	Pd(OAc) ₂ , neat, rt	(81)	—	80
Et	Me	[(Cp)Fe(CO) ₂ (THF)]*BF ₄ ⁻ , CH ₂ Cl ₂ , 40°	(66)	40:60	322
Et	Me	RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(91)	65:35	52, 338
Et	Me	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(91)	63:37	52
Et	Me	RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(83)	67:33	52
Et	Me	Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(90)	65:35	52
Et	Me	OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(61)	64:36	338
Et	Me	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(90)	60:40	351
Et	Me	(7-PPh ₂ -8-Me-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(93)	58:42	351
Et	Me	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀) Rh(1,5-cyclooctadiene), neat, 4 h, 100°	(94)	59:41	351
Et	Me	[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(96)	66:34	81
Et	Me	[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(96)	65:35	81
Et	Me	RuCl(<i>p</i> -cymene)(TsNC ₆ H ₄ NH ₂) ₂ , neat, 80°	(93)	65:35	357
Et	Me	[Ru(<i>meso</i> -tetraphenylporphyrin)- (CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(58)	92:8	370
Et	Me	[Ru(<i>meso</i> -tetramesitylporphyrin)- (CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(66)	88:12	370
Et	Me	[Ru(octaethylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(36)	91:9	370
Et	Me	[Ru(tetrapropylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(52)	91:9	370
Et	Me	13a , neat, 60°, 4 h	(73)	75:25	364
Et	Me	13d , neat, 60°, 4 h	(67)	69:31	364
Et	Me	14a , neat, 60°, 4 h	(65)	77:23	364
Et	Me	14d , neat, 60°, 4 h	(59)	86:14	364
Et	Me	14f , neat, 60°, 4 h	(52)	86:14	364
Et	Me	23b , neat, 60°, 4 h	(74)	63:37	340
Et	Me	24b , neat, 60°, 4 h	(70)	69:31	340
Et	OMe	Pd(OAc) ₂	(—)	—	376
Et	OMe	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(61)	65:35	91
Et	OMe	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(84)	62:38	91
Et	OMe	Pd(OAc) ₂ , neat, rt	(79)	—	80
Et	OMe	Iron <i>meso</i> -tetra- <i>p</i> -tolylporphyrin chloride, CH ₂ Cl ₂ , 40°, 5 h	(—)	85:15	57

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
Et	OMe	Iron <i>meso</i> -tetra(pentafluorophenyl)-porphyrin chloride, CH ₂ Cl ₂ , rt, 7 h	(—)	85:15	57
Et	OMe	Iron <i>meso</i> -tetramesitylporphyrin-chloride/cobaltocene, CH ₂ Cl ₂ , rt, 3 h	(—)	92:8	57
Et	OMe	RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(92)	61:39	52, 338
Et	OMe	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(87)	59:41	52
Et	OMe	RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(87)	62:38	52
Et	OMe	Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(90)	61:39	52
Et	OMe	OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(59)	62:38	338
Et	OMe	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(87)	62:38	351
Et	OMe	[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(90)	62:38	81
Et	OMe	[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(89)	64:36	81
Et	OMe	RuCl(<i>p</i> -cymene)(TsNC ₆ H ₄ NH ₂ -2), neat, 80°	(87)	70:30	357
Et	OMe	Hydridotris(3,5-Me ₂ -1-pyrazolyl)-borateCu(C ₂ H ₄), DCE, rt	(—)	58:42	365
Et	OMe	[Ru(<i>meso</i> -tetraphenylporphyrin)-(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(71)	89:11	370
Et	OMe	[Ru(<i>meso</i> -tetramesitylporphyrin)-(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(81)	88:12	370
Et	OMe	[Ru(octaethylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(41)	85:15	370
Et	OMe	[Ru(tetrapropylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(44)	88:12	370
Et	OMe	23b , neat, 60°, 4 h	(72)	68:32	340
Et	OMe	24b , neat, 60°, 4 h	(68)	69:31	340
Et	Et	Pd(OAc) ₂	(—)	—	376
Et	OEt	Pd(OAc) ₂	(—)	—	376
Et	CO ₂ Et	Pd(OAc) ₂	(—)	—	376
Et	NMe ₂	Pd(OAc) ₂ , neat, rt	(0)	—	80
Et	<i>i</i> -Pr	Pd(OAc) ₂	(—)	—	376
Et	<i>t</i> -Bu	Rh ₂ (O ₂ CH) ₄ , 60°	(—)	53:47	325
Et	<i>t</i> -Bu	Rh ₂ (OAc) ₄ , 60°	(—)	57:43	325
Et	<i>t</i> -Bu	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 60°	(—)	58:42	325
Et	<i>t</i> -Bu	Pd(OAc) ₂	(—)	—	376
Et	<i>t</i> -Bu	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(57)	62:38	91
Et	<i>t</i> -Bu	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(79)	60:40	91
Et	<i>t</i> -Bu	Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(88)	58:42	51
Et	<i>t</i> -Bu	Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(77)	60:40	51
Et	<i>t</i> -Bu	ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(89)	57:43	51
Et	<i>t</i> -Bu	RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(90)	58:42	52, 338
Et	<i>t</i> -Bu	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(87)	64:36	52
Et	<i>t</i> -Bu	RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(83)	64:36	52
Et	<i>t</i> -Bu	Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(85)	63:37	52
Et	<i>t</i> -Bu	OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(49)	57:43	338
Et	<i>t</i> -Bu	(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(93)	65:35	351
Et	<i>t</i> -Bu	[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(93)	67:33	81
Et	<i>t</i> -Bu	[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(91)	68:32	81
Et	<i>t</i> -Bu	RuCl(<i>p</i> -cymene)(TsNC ₆ H ₄ NH ₂ -2), neat, 80°	(88)	67:33	357
Et	<i>t</i> -Bu	23b , neat, 60°, 4 h	(67)	65:35	340
Et	<i>t</i> -Bu	24b , neat, 60°, 4 h	(65)	70:30	340

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et				
		Cu, xylene, 120°	<i>trans:cis</i> (42) —	377
		(CO) ₂ WC(OMe)Ph, 35°	(28) 55:45	321
		Rh ₂ (OAc) ₄ , neat, rt	(92) 58:42	71
R = Et		CuSO ₄ , heptane, 70°	(55)	378
R = Et		Cu-bronze, benzene, reflux, 24 h	(50)	379
R = Et		Rh ₂ (OAc) ₄	(24)	380
R = Et		Rh ₂ (OAc) ₄	(78)	380, 381
C ₃ R = Me		Catalyst, neat, rt, 10 h		
		Catalyst		
		Rh ₂ (OAc) ₄	(64)	77, 80
		Rh ₂ (OPiv) ₄	(60)	77
		Cu(OTf) ₂	(25)	77, 80
		Pd(OAc) ₂	(10)	77, 80
R Me		CuSO ₄ , neat, 80°	(56)	382
C ₄ Et		Cu(acac) ₂ , benzene, reflux	(89)	41
R = Et		Cu-bronze, methylcyclohexane, reflux, 14 h	(—) <i>trans:cis</i> = 70:30	329
C ₃ R = Me		Cu(acac) ₂ , benzene, 90°	(75)	312

TABLE I. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)


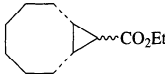

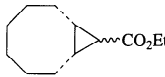
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₄ R = Et			<u>exo:endo</u>		
			(—)	58:42	325
		Rh ₂ (O ₂ CH) ₄ , 60°	(—)	58:42	325
		Rh ₂ (OAc) ₄ , 60°	(—)	56:44	325
		Rh ₂ (OAc) ₄ , neat, rt	(95)	—	80
		Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 60°	(—)	57:43	325
		Cu(OTf) ₂ , neat, rt	(28)	—	80
		Pd(OAc) ₂ , neat, rt	(20)	—	80
		[Rh(PE-CO ₂) ₂] ₂ , toluene, 100°	(80)	78:22	367
		CuSO ₄ , neat, rt to 135°	(—)	33:67	383
		[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(13)	41:59	91
		[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(26)	46:54	91
		OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(1)	53:47	338
		Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(91)	63:37	51
		Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(16)	47:53	51
		ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₉), neat, 60°	(87)	51:49	51
		RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(5)	61:39	52, 338
		RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(6)	58:42	52
		RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(4)	65:35	52
		Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(4)	65:35	52
		(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(86)	59:41	351
		(7-PPh ₂ -8-Me-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(85)	60:40	351
		(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)-Rh(PPh ₃) ₂ , neat, 4 h, 100°	(88)	58:42	351
		Rh(1,5-cyclooctadiene), neat, 4 h, 100°			
		Pt(PPh ₃) ₄ , neat, 100°	(42)	73:27	368
		PtCl ₂ , neat, 100°	(39)	68:32	368
		[PtCl ₂ (cyclohexene)] ₂ , neat, 100°	(54)	67:33	368
		<i>cis</i> -PtCl ₂ (benzonitrile) ₂ , neat, 100°	(54)	66:34	368
		<i>cis</i> -PtCl ₂ (pyr) ₂ , neat, 100°	(22)	83:17	368
		<i>cis</i> -PtCl ₂ (PPh ₃) ₂ , neat, 100°	(29)	67:33	368
		<i>trans</i> -PtCl ₂ (PPh ₃) ₂ , neat, 100°	(33)	65:35	368
		PtBr ₂ , neat, 100°	(29)	72:28	368
		PtI ₂ , neat, 100°	(54)	66:34	368
		PtI ₂ (NH ₃) ₂ , neat, 100°	(31)	74:26	368
		PtCl ₄ , neat, 100°	(71)	64:36	368
		PtBr ₄ , neat, 100°	(42)	74:26	368
		[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(51)	54:46	81
		[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(65)	48:52	81
R = Et			<u>exo:endo</u>		
			Catalyst, neat		357
		Catalyst	Temp		
		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂]	60°	(34)	58:42
		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂]	100°	(66)	60:40
		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂]	60°	(10)	61:39
		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂]	100°	(89)	53:47
		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂]	60°	(12)	65:35
		RuCl(<i>p</i> -cymene)[TsN(CH ₂) ₂ NH ₂]	100°	(58)	65:35
		RuCl(<i>p</i> -cymene)[TsN- <i>o</i> -NH ₂ Ph]	60°	(52)	51:49
		RuCl(<i>p</i> -cymene)[TsN- <i>o</i> -NH ₂ Ph]	100°	(83)	61:39
		RuCl(<i>p</i> -cymene)[2-TsNpyridine]	60°	(20)	59:41
		RuCl(<i>p</i> -cymene)[2-TsNpyridine]	100°	(88)	59:41
		RuCl(<i>p</i> -cymene)[2-(TsNCH ₂)pyridine]	60°	(45)	73:27
		RuCl(<i>p</i> -cymene)[2-(TsNCH ₂)pyridine]	100°	(82)	56:44

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et				
			<i>exo:endo</i>	
		Hydridotris(3,5-dimethyl-1-pyrazolyl)-borateCu(C ₂ H ₄), DCE, rt	(78) 99:1	348
		Ru ₂ (OAc) ₄ (MeOH) ₂ , neat, 60°	(12) 68:32	384
		Ru ₂ (O ₂ CCF ₃) ₄ , neat, 60°	(99) 38:62	384
		RuCl ₂ (PPh ₃) ₃ , neat, 60°	(82) 62:38	384
		[(C ₆ H ₆)RuCl ₂] ₂ , neat, 60°	(42) 62:38	384
		[(<i>p</i> -cymene)RuCl ₂] ₂ , neat, 60°	(44) 60:40	384
		(<i>p</i> -cymene)RuCl ₂ •PPh ₃ , neat, 60°	(43) 67:33	384
		(<i>p</i> -cymene)RuCl ₂ •(<i>p</i> -cymene) ₃ , neat, 60°	(0) —	384
		23a , neat, 60°, 4 h	(47) 59:41	340
		23b , neat, 60°, 4 h	(51) 65:35	340
		24a , neat, 60°, 4 h	(19) 60:40	340
		24b , neat, 60°, 4 h	(8) 65:35	340
R = Et		CuCl•PMe ₃ , neat, reflux	(51)	337
R = Et		Cu(acac) ₂ , benzene, 85°	(48)	295
R = Et		Catalyst, neat, 60°, 4 h		340
		Catalyst	<i>trans:cis</i>	
		23b	(46) 56:44	
		24b	(9) 60:40	
C ₃		Rh ₂ (OAc) ₄ , neat, rt	(65)	80, 77
		Rh ₂ (O ₂ CC ₃ H ₇ - <i>n</i>) ₄ , neat, rt, 10 h	(80)	77
		Rh ₂ (OPiv) ₄ , neat, rt, 10 h	(89)	77
		Cu(OTf) ₂ , neat, rt	(40)	80, 77
		Pd(OAc) ₂ , neat, rt	(5)	80, 77
C ₄	CH ₂ CH ₂ Cl	CuSO ₄ , neat, 100°	(15)	341
C ₆	<i>n</i> -Bu	Rh ₂ (OAc) ₄ , neat, rt	(90)	80, 77
C ₃		Rh ₂ (OAc) ₄ , neat, rt	(24)	80, 77
		Rh ₂ (OPiv) ₄ , neat, rt, 10 h	(77)	77
		Cu(OTf) ₂ , neat, rt	(14)	80, 77
		Pd(OAc) ₂ , neat, rt	(2)	80, 77
C ₆	<i>n</i> -Bu	Rh ₂ (OAc) ₄ , neat, rt	(70)	80, 77
C ₄	R = Et	MeReO ₃ , neat	(59)	319

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst, neat, rt, 10 h		77
		<u>Catalyst</u>		
C ₃	R	Rh ₂ (OAc) ₄	(7)	
	Me	Rh ₂ (O ₂ CC ₃ H _{7-n}) ₄	(54)	
	Me	Rh ₂ (OPiv) ₄	(60)	
	Me	Cu(OTf) ₂	(8)	
	Me	Pd(OAc) ₂	(12)	
C ₄	Et	Cu(OTf) ₂	(23)	
C ₆	n-Bu	Rh ₂ (OAc) ₄	(70)	
	n-Bu	Rh ₂ (OPiv) ₄	(85)	
C ₄	R = Et 	Cu-bronze, CuSO ₄ , 118°	(59)	385
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt		309
			<u>trans:cis</u>	
C ₃	Me		(54) 62:38	
C ₆	t-Bu		(49) 67:33	
C ₄	R = Et 	CuSO ₄ , cyclohexane, reflux, 12 h	(—)	293
			+	
			<u>E:Z</u>	
C ₃	Me	Cu(acac) ₂ , 100°, 3 h	(67) —	307
	Me	[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , rt	(91) 40:60	308
C ₄	Et	Rh ₂ (O ₂ CH) ₄ , 60°	(—) 49:51	325
	Et	Rh ₂ (OAc) ₄ , 60°	(—) 50:50	325
	Et	Rh ₂ (O ₂ CPr- <i>n</i>) ₄ , 60°	(—) 50:50	325
	Et	[Rh(PE-CO ₂) ₂] ₂ , toluene, 100°	(96) 62:38	367
	Et	MeReO ₃ , neat	(60) 60:40	319
	Et	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 60°	(62) 40:60	91
	Et	[OsCl ₂ (<i>p</i> -cymene)] ₂ , neat, 80°	(79) 41:59	91
	Et	Cl(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₁₀), neat, 60°	(81) 50:50	51
	Et	Cl(Ph ₃ P) ₂ Ru(Me ₂ C ₂ B ₉ H ₁₀), neat, 60°	(73) 42:58	51
	Et	ClH(Ph ₃ P) ₂ Ru(H ₂ C ₂ B ₉ H ₇), neat, 60°	(87) 50:50	51
	Et	Pd(OAc) ₂ , neat, rt	(42) —	80
	Et	Iron <i>meso</i> -tetra- <i>p</i> -tolylporphyrin chloride, CH ₂ Cl ₂ , rt, 1 h	(—) 81:19	57
	Et	Iron <i>meso</i> -tetra- <i>p</i> -tolylporphyrin chloride, CH ₂ Cl ₂ , 40°, 18 h	(—) 77:23	57
	Et	Iron <i>meso</i> -tetra-(pentafluorophenyl)porphyrin chloride, CH ₂ Cl ₂ , rt, 3 h	(—) 52:48	57
	Et	Iron <i>meso</i> -tetramesitylporphyrin chloride/cobaltocene, CH ₂ Cl ₂ , rt, 8 h	(—) 75:25	57
	Et	Iron octaethylporphyrin chloride/cobaltocene, CH ₂ Cl ₂ , rt, 4 h	(—) 79:21	57
	Et	Osmium <i>meso</i> -tetra- <i>p</i> -tolylporphyrin(CO)(pyr), toluene, rt, 2 h	(39) 74:26	90
	Et	[(Cp)Fe(CO) ₂ (THF)] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , 40°	(60) 40:60	322
	Et	(7-Ph ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(94) 53:47	351

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)


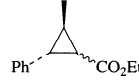
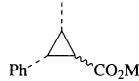
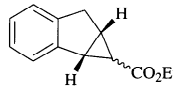

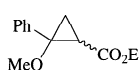
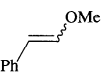
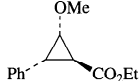
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Et		RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(94) 53:47	338
Et		OsCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(55) 51:49	338
Et		[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(98) 51:49	81
Et		[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(97) 50:50	81
Et		RuCl(<i>p</i> -cymene)(TsNC ₆ H ₄ NH ₂ -2), neat, 80°	(92) 51:49	357
Et		Cu/bronze-K10 montmorillonite, CH ₂ Cl ₂ , rt	(—) 44:56	339
Et		Cu/bronze-bentonite, CH ₂ Cl ₂ , rt	(—) 55:45	339
Et		[Ru(<i>meso</i> -tetraphenylporphyrin)(CO)], neat, rt, 4 h	(—) 76:24	84
Et		[Ru(<i>meso</i> -tetramesitylporphyrin)(CO)], neat, rt, 4 h	(—) 62:38	84
Et		[Ru(<i>meso</i> -tetramesitylporphyrin)(O ₂)], neat, rt, 4 h	(—) 60:40	84
Et		[Ru(<i>meso</i> -tetraphenylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(50) 74:26	370
Et		[Ru(<i>meso</i> -tetramesitylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(68) 63:37	370
Et		[Ru(octaethylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(36) 67:33	370
Et		[Ru(tetrapropylporphyrin)(CO)(EtOH)], CH ₂ Cl ₂ , rt, 8 h	(23) 73:27	370
Et		RuCl ₂ (PPh ₃) ₃ , neat, 60°, 4 h	(94) 53:47	52
Et		RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆ , neat, 60°, 4 h	(90) 53:47	52
Et		RuH ₃ [Si(OEt) ₃](PPh ₃) ₂ , neat, 60°, 4 h	(86) 53:47	52
Et		Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂ , neat, 60°, 4 h	(92) 51:49	52
Et		23b , neat, 60°, 4 h	(82) 58:42	340
Et		24b , neat, 60°, 4 h	(78) 65:35	340
C ₁₂	<i>l</i> -menthyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	(80) 53:47	309
	<i>d</i> -menthyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	()	309
				
	R		<i>trans:cis</i>	
C ₃	Me	Cu(acac) ₂ , 100°, 3 h	(59) —	307
C ₄	Et	Osmium <i>meso</i> -tetra- <i>p</i> -tolylporphyrin-(CO)(pyr), toluene, rt, 2 h	(13) —	90
	Et	RuCl(<i>p</i> -cymene)(TsNC ₆ H ₄ NH ₂ -4), neat, 80°	(89) 69:31	357
C ₆	<i>t</i> -Bu	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	(10) 92:8	309
C ₃	R = Me	Cu(acac) ₂ , 100°, 3 h	(68) —	307
				
C ₄	R = Et			326
			<i>exo:endo</i>	
		Cu(OSO ₂ CF ₃)	(53) 68:32	
		4	(61) 99:1	
		5	(72) 97:3	
		6	(61) 98:2	
R = Et				
			<i>trans:cis</i>	
		Rh ₂ (OAc) ₄ , Et ₂ O, rt	(94) 50:50	94, 71
		Cu, 115°, 1 h	(91) —	352
		MeReO ₃ , neat	(87) —	319
R = Et		CuSO ₄	(23) —	387
				

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

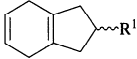
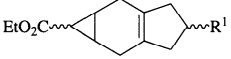
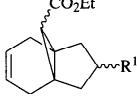
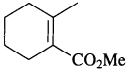
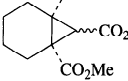
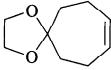
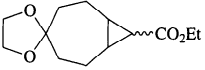
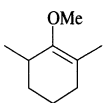
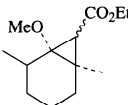
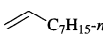

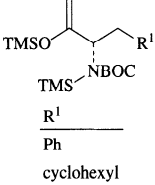
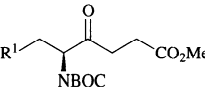
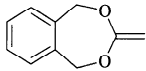
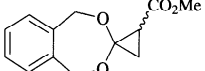
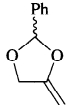
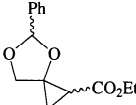

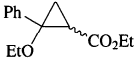
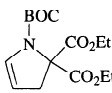
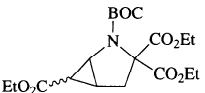
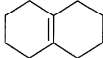
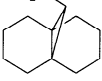

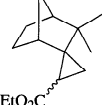
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		CuSO ₄ , neat, 110°, 3 h	EtO ₂ C-  -R ¹ +  I I:II (70) 71:29 (75) 80:20 II	388
R = Et		Cu-bronze, heat	 (—) <i>exo:endo</i> = 2:1	380
R = Et		Cu, 110°, 30 min	 (52)	389
R = Et		Cu-bronze, methylcyclohexane, reflux, 7 h	 (—) mixture of stereoisomers = 70:30	329
R = Et		[Rh(PE-CO ₂) ₂] ₂ , toluene, 100°	RO ₂ C-  -C ₇ H _{15-n} (79) <i>trans:cis</i> = 63:37	367
C ₃ R = Me		1. Cu(acac) ₂ , benzene, 80° 2. Bu ₄ NF, CH ₂ Cl ₂	 (37) (50)	390
R = Me		Rh ₂ (OAc) ₄	 (67)	289
C ₄ R = Et		CuSO ₄ , heptane, 70°	 (66)	378
R = Et		CuSO ₄ , neat, 60° Cu, 115°, 1 h	 (—) (93)	245 352
R = Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 12 h	 (46)	391
R = Et		[Cu(MeCN) ₄] ⁺ BF ₄ ⁻ , CH ₂ Cl ₂ , rt, 10 min	 (7)	317
R = Et		CuSO ₄ , cyclohexane, reflux, 10 h	 (79)	392

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		Cu(acac) ₂ , benzene, 90°	 (—)	393
C ₃ R = Me		Cu(acac) ₂ , ethyl acetate, 100°	 (74)	294
C ₁₂ R = <i>d,l</i> -menthyl		Cu(acac) ₂ , cyclohexane, 40°	 (88)	394
C ₄ R = Et		CuSO ₄ , 100° Osmium <i>meso</i> -tetra- <i>p</i> -tolylporphyrin-(CO)(pyr), toluene, rt, 2 h 23b , neat, 60°, 4 h 24b , neat, 60°, 4 h	 <i>trans:cis</i> (59) — (32) 81:19 (42) 58:42 (8) 64:36	347 90 340 340
R = Et		Rh ₂ (OAc) ₄ , Et ₂ O	 (—)	395
R = Et		Iodorhodium(III)- <i>meso</i> -tetra- <i>p</i> -tolylporphyrin	 (—)	56
R = Et		CuSO ₄ , 110°	 (25)	396
R = Et		Cu, 115°, 1 h	 (90)	352
R = Et		Cu, 115°, 1 h	 (88)	352
R = Et		Cu powder	 (36)	397
R = Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	 <i>trans:cis</i> (56) 63:37 (49) 62:38	309
C ₆ R = <i>t</i> -Bu				

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ R = Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 1 h	(43)	324
R = Et		CuSO ₄ , 80°	(59) <i>trans:cis</i> = >95:5	398
C ₃ R = Me		CuSO ₄ , neat, 0°	(76)	399
C ₄ R = Et		CuSO ₄ , benzene	(65)	210
R = Et		CuCl·P(OEt) ₃ , hexane, rt, 1.5 h	(30)	400
R = Et		CuSO ₄ , 100°	(63) <i>trans:cis</i> —	347
		23b , neat, 60°, 4 h	(44) 58:42	340
		24b , neat, 60°, 4 h	(12) 67:33	340
		(7-PPh ₂ -8-H-7,8-C ₂ B ₉ H ₁₀)Rh(PPh ₃) ₂ , neat, 4 h, 100°	(73) 60:40	351
		[RuH(7-PPh ₂ -8-H-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(59) 58:42	81
		[RuH(7-PPh ₂ -8-Me-C ₂ B ₉ H ₁₀)(PPh ₃) ₂], neat, 100°	(61) 58:42	81
R = Et		Rh ₂ (OAc) ₄	(70) + (20)	401
R = Et		CuSO ₄ , neat, 90°, 2 h	(50)	402
R = Et		Rh ₂ (OAc) ₄	(90)	214
R = Et		CuSO ₄ , benzene, 90°	(70) <i>exo:endo</i> = 80:20	403

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
R = Et		CuSO ₄ , neat, 90°, 2 h	 (50)	404																																			
R = Et		Iodorrhodium(III)- <i>meso</i> -tetraphenylporphyrin, neat, 60°	 (51)	102, 101																																			
R = Et		1. CuSO ₄ , benzene 2. Saponification	 (55)	405																																			
C ₁₂	R = <i>l</i> -menthyl	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	 (63)	309																																			
C ₄	R = Et	1. CuSO ₄ , benzene 2. Saponification	 (81)	405																																			
R = Et		Hydridotris(3,5-dimethyl-1-pyrazolyl)borateCu(C ₂ H ₄), DCE, rt	 (0)	348																																			
R = Et		1. CuSO ₄ , benzene 2. Saponification	 (77)	405																																			
R Et C ₆ <i>t</i> -Bu		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt	 <i>trans:cis</i> (55) 60:40 (51) 67:33	309																																			
C ₄	R = Et	1. CuSO ₄ , benzene, 75°, 4 h 2. NaOH/MeOH/H ₂ O, 50°	 (21)	406																																			
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>(21)</td></tr> <tr><td>Me</td><td>Me</td><td>(71)</td></tr> <tr><td>OMe</td><td>OMe</td><td>(50)</td></tr> <tr><td>Cl</td><td>Cl</td><td>(50)</td></tr> <tr><td>H</td><td>Me</td><td>(30)</td></tr> <tr><td>H</td><td>Cl</td><td>(14)</td></tr> <tr><td>H</td><td>CF₃</td><td>(8)</td></tr> <tr><td>Me</td><td>Cl</td><td>(50)</td></tr> <tr><td>Me</td><td>CF₃</td><td>(6)</td></tr> <tr><td>CF₃</td><td>CF₃</td><td>(<1)</td></tr> <tr><td>Br</td><td>Me</td><td>(38)</td></tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	H	(21)	Me	Me	(71)	OMe	OMe	(50)	Cl	Cl	(50)	H	Me	(30)	H	Cl	(14)	H	CF ₃	(8)	Me	Cl	(50)	Me	CF ₃	(6)	CF ₃	CF ₃	(<1)	Br	Me	(38)
R ¹	R ²	Yield (%)																																					
H	H	(21)																																					
Me	Me	(71)																																					
OMe	OMe	(50)																																					
Cl	Cl	(50)																																					
H	Me	(30)																																					
H	Cl	(14)																																					
H	CF ₃	(8)																																					
Me	Cl	(50)																																					
Me	CF ₃	(6)																																					
CF ₃	CF ₃	(<1)																																					
Br	Me	(38)																																					
R = Et		Cu bis[<i>N</i> -(<i>R,S</i>)- α -PhEt-salicylaldiminate], benzene, 80°	 (68)	407																																			
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>(68)</td></tr> <tr><td>Me</td><td>H</td><td>(67)</td></tr> <tr><td>H</td><td>Me</td><td>(65)</td></tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	H	(68)	Me	H	(67)	H	Me	(65)																								
R ¹	R ²	Yield (%)																																					
H	H	(68)																																					
Me	H	(67)																																					
H	Me	(65)																																					

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
R = Et		Cu(acac) ₂ , THF, 65°, 9 h	(45)	408								
R = Et		CuSO ₄ , 100°	(65)	347								
R = Et		Rh ₂ (OAc) ₄	(75)	401								
R = Et	 <table style="margin-left: auto; margin-right: auto;"> <tr><td>R¹</td></tr> <tr><td>H</td></tr> <tr><td>Me</td></tr> </table>	R ¹	H	Me	Cu bis[<i>N</i> -(<i>R,S</i>)- α -PhEt-salicylaldimine], benzene, 80°	(60) (14)	407					
R ¹												
H												
Me												
R = Et		CuSO ₄	(—)	409								
R = Et		Rh ₂ (OAc) ₄ , Et ₂ O/THF	(63) <i>E:Z</i> = 50:50	410								
C ₆	R = <i>t</i> -Bu 	CuSO ₄ , neat, 90°	(44)	411								
C ₄	R = Et 	CuSO ₄ , 100°	(69)	347								
R = Et		CuSO ₄	(70) <i>I:II</i> = 67:33	211								
R = Et	 <table style="margin-left: auto; margin-right: auto;"> <tr><td>R¹</td><td>R²</td></tr> <tr><td>H</td><td>H</td></tr> <tr><td>Me</td><td>H</td></tr> <tr><td>H</td><td>Me</td></tr> </table>	R ¹	R ²	H	H	Me	H	H	Me	Cu-bis[<i>N</i> -(<i>R,S</i>)- α -PhEt-salicylaldimine], benzene, 80°	(69) (77) (62)	407
R ¹	R ²											
H	H											
Me	H											
H	Me											
R = Et		Bis(<i>N</i> -benzylsalicylaldimine)Cu(II), benzene, 85°	(65)	412								

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 18 h	(92) 413	
R = Et		Cu•P(OMe) ₃ , neat, rt	(74) 414	
C ₃		Cu-bronze, 80°	(54) 95	
		Cu(acac) ₂ , 60°	(40) 415	
	$\frac{R}{\text{Mc}}$ Ac	Cu-bronze, neat, 90°, 5 h Cu-bronze, cyclohexane, reflux, 10 h	(—) (—)	416 416
C ₄		Cu, CH ₂ Cl ₂ , 0°	(14) 453	
		Cu, CH ₂ Cl ₂ , 0°	(39) 453	
		Cu, CH ₂ Cl ₂ , 0°	(67) 453	
		Cu, CH ₂ Cl ₂ , 0°	(55) 453	
C ₄		Cu(acac) ₂ , neat, 75°	(35) 418	
		Cu-bronze, MeC ₆ H ₁₁ -c, reflux, 2 h	(77) 419	
C ₅	$\frac{R}{\text{H}}$ Me Ph <i>p</i> -MeOC ₆ H ₄	1. Rh ₂ (OAc) ₄ , Et ₂ O, reflux, 4 h 2. HCl/THF	(73) (83) (90) (94)	420
		Rh ₂ (OAc) ₄ , Et ₂ O, 35°	(34) Z:E = 32:68	196

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Rh ₂ (OAc) ₄ , Et ₂ O, reflux, 4 h 2. HCl/THF	 (77)	420
		Cu(acac) ₂ , neat, reflux	 I + II (-) I:II = 6:1	418
		Cu(acac) ₂ , neat, reflux	 I + II (-) I:II = 7:1	418
		Cu-bronze	 (66)	68
		CuOTf, CH ₂ Cl ₂ , 5°	 (62)	98, 421
		CuOTf, CH ₂ Cl ₂ , 5°	 (71)	98, 421
		CuOTf, CH ₂ Cl ₂ , 5°	 (79)	98, 421
		CuOTf, CH ₂ Cl ₂ , 5°	 (64)	98, 421
		CuOTf, CH ₂ Cl ₂ , 5°	 (73)	98, 421
		CuOTf, CH ₂ Cl ₂ , 5°	 (53)	98, 421
C₆		Cu(acac) ₂ , neat, 60°	 (51)	422
		Cu(acac) ₂ , neat, 60°	 (45)	422
		Rh ₂ (OAc) ₄ , neat, 75°	 (63)	417
		Cu(acac) ₂ , neat, 75°	 (79)	417
		Cu(acac) ₂ , neat, 60°	 (65)	422

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu(acac) ₂ , neat, 60°	 (57)	422
		Cu(acac) ₂ , neat, 75°	 (64)	417
		Cu(acac) ₂ , benzene, 60°	 (60)	422
		Cu(acac) ₂ , neat, 60°	 (53)	422
		Cu(acac) ₂ , neat, 60°	 (55)	422
		Cu(acac) ₂ , Et ₂ O, 75°	 (46)	417
		Cu(acac) ₂ , neat, 60°	 (50)	422
		Cu(acac) ₂ , neat, 60°	 (49)	422
		Cu(acac) ₂ , benzene, 60°	 (61)	422
		[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , 83°	 (54) <i>trans:cis</i> = 88:12	308
		[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , 63°	 (89) <i>trans:cis</i> = 77:23	308
		[Ru ₂ (CO) ₄ (μ-OAc) ₂] _n , CH ₂ Cl ₂ , 70°	 (70) <i>trans:cis</i> = 64:36	308
		1. Cu(acac) ₂ , neat, rt 2. HCl, Et ₂ O, rt	 (>95)	423
		1. Cu(acac) ₂ , neat, 33° 2. HCl, Et ₂ O, rt	 (>95)	423
		1. Cu(acac) ₂ , neat, 33° 2. HCl, Et ₂ O, rt	 (>95)	423

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
		Cu(acac) ₂ , neat, 60°	 (75)	423	
C ₈		Mo(CO) ₆ , neat			
			<u>Temp</u> <u>Time</u>	<u>trans:cis</u>	
		H	rt 70 h	(63) 69:31	298
		H	65° 7 h	(77) 69:31	298, 299
		Me	rt 72 h	(19) 55:45	298
Me	65° —	(58) 55:45	298, 299		
		Mo(CO) ₆ , neat, 65°	 (52) <i>trans:cis</i> = 71:29	299	
		Mo(CO) ₆ , neat	 <u>Temp</u> <u>Time</u>		
		rt 70 h	(48) 57:43	298	
		65° 8 h	(72) 63:37	298, 299	
		Mo(CO) ₆ , neat, 65°	 (85) <i>trans:cis</i> = 66:34	299	
		CuX, 80°, 20 min	 <u>X</u>	424	
		I	(55-57)		
		O	(51-53)		
		Cu, neat, 120°, 2 h	 (—)	425	
		Rh ₂ (OAc) ₄ , DME, rt, 3 h	 (37)	426	
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (75)	426	
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (74)	426	
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (31)	426	

TABLE 1. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Rh ₂ (OPiv) ₄ , DME, rt, 5 h Rh ₂ (OPiv) ₄ , DME, 80°, 4 h Pd(OAc) ₂ , DME, rt, 4 h	 (22) (21) (0)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h Rh ₆ (CO) ₁₆ , DME, rt, 4 h	 (6) (2)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (30)	426
		Rh ₂ (OAc) ₄ , DME, rt, 1 h	 (31)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (83)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (44)	426
		Rh ₂ (OAc) ₄ , DME, rt, 3 h Rh ₂ (OPiv) ₄ , DME, rt, 4 h CuCl, P(OMe) ₃ , DME, rt, 3 h	 (30) (56) (6)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (64)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (68)	426
		Rh ₂ (OAc) ₄ , DME, rt, 4 h Rh ₂ (OPiv) ₄ , DME, rt, 4 h Rh ₂ (OPiv) ₄ , DME, 85°, 4 h Rh ₆ (CO) ₁₆ , DME, rt, 12 h Cu(BSI) ₂ , DME, rt, 12 h	 (51) (59) (9) (14) (5)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (54)	426

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Rh ₂ (OPiv) ₄ , DME, rt, 2.5 h	 (13)	426
		Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (18)	426
		Rh ₂ (OAc) ₄ , DME, rt, 4 h Rh ₂ (OPiv) ₄ , DME, rt, 4 h	 (42) (55)	426
		Pd(OAc) ₂ , neat, reflux, 1.5 h	 (63)	427
		Rh ₂ (OAc) ₄ Pd(OAc) ₂	 (71) (37)	428, 429
		(Bu ₂ S) ₂ CuI, 5-10°	 (56)	424
		Cu-bronze, 80°	 (71)	95
		Rh ₂ (OAc) ₄	 (71) (-)	95
C₉ 		Cu(acac) ₂	 (37)	430
		Pd(OAc) ₂ , neat, reflux, 2.5 h	 (49)	427
		Rh ₂ (OAc) ₄	 (65)	428
		Rh ₂ (OAc) ₄ , Et ₂ O, rt, 4 h Pd(OAc) ₂ CuCl	 (70) (72) (30)	428, 429

TABLE 1. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)

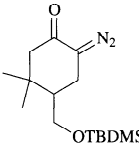

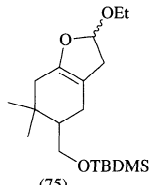
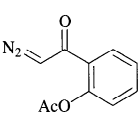

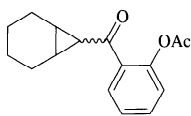
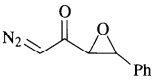

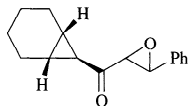
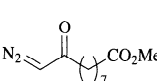
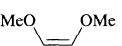
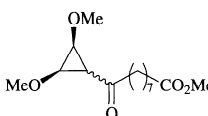
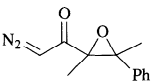

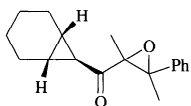
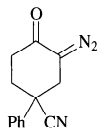

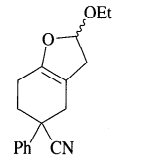
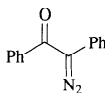

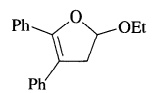
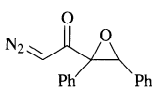

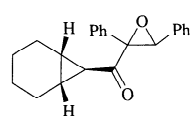
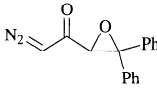

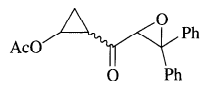


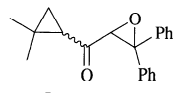


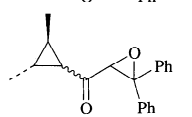
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		$\text{Rh}_2(\text{OAc})_4$ $\text{Pd}(\text{OAc})_2$ CuCl	 (75) (72) (35)	428, 429
C₁₀ 		$\text{Rh}_2(\text{OAc})_4$, benzene	 (50)	431
		$\text{Pd}(\text{OAc})_2$, neat, reflux, 0.5 h	 (33)	427
C₁₁ 		Cu-bronze, 80°	 (76)	95
C₁₂ 		$\text{Pd}(\text{OAc})_2$, neat, reflux, 5.5 h	 (39)	427
C₁₃ 		$\text{Rh}_2(\text{OAc})_4$ $\text{Pd}(\text{OAc})_2$ CuCl	 (40) (36) (10)	428, 429
C₁₄ 		$\text{Rh}_2(\text{OAc})_4$, neat $\text{Rh}_2(\text{OAc})_4$, Et ₂ O $\text{Rh}_2(\text{OAc})_4$, pentane $\text{Rh}_2(\text{OPiv})_4$, pentane	 (68) (97) (91) (93)	429 429 429, 428 429, 428
C₁₆ 		$\text{Pd}(\text{OAc})_2$, neat, reflux, 0.5 h	 (41)	427
		$\text{Pd}(\text{OAc})_2$, neat, reflux, 30 min	 (—)	427
		$\text{Pd}(\text{OAc})_2$, neat, sealed tube, 85°, 6 h	 (48)	427
		$\text{Pd}(\text{OAc})_2$, neat, sealed tube, 85°, 7 h	 (41)	427

TABLE I. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETATES AND RELATED SYSTEMS (Continued)


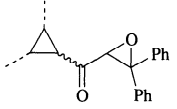

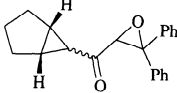

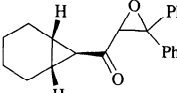

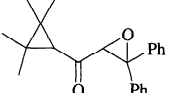

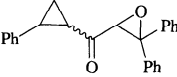
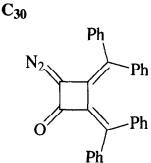

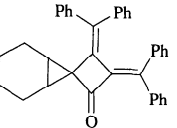
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ , neat, sealed tube, 85°, 7 h	 (38) <i>trans:cis</i> = 67:33	427
		Pd(OAc) ₂ , neat, reflux, 6 h	 (25) <i>exo:endo</i> = 83:17	427
		Pd(OAc) ₂ , neat, reflux, 5 h	 (54)	427
		Pd(OAc) ₂ , neat, reflux, 6 h	 (—)	427
		Pd(OAc) ₂ , CH ₂ Cl ₂ , rt, 10 days	 (16)	427
 C ₃₀		Cu, heat, 20 min	 (60)	432

TABLE II. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS



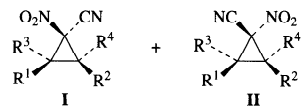


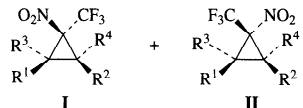
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																						
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂		433																																						
					<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>I+II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>H</td> <td>(50)</td> <td>—</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> <td>(40)</td> <td>94:6</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>Me</td> <td>(30)</td> <td>—</td> </tr> <tr> <td>—(CH₂)₄—</td> <td>H</td> <td>H</td> <td>H</td> <td>(40)</td> <td>>95:5</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>Me</td> <td>(35)</td> <td>—</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>H</td> <td>(55)</td> <td>67:33</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	I+II	I:II	Me	H	Me	H	(50)	—	Me	Me	H	H	(40)	94:6	Me	H	H	Me	(30)	—	—(CH ₂) ₄ —	H	H	H	(40)	>95:5	Me	Me	Me	Me	(35)	—	Ph
R ¹	R ²	R ³	R ⁴	I+II	I:II																																					
Me	H	Me	H	(50)	—																																					
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R ¹	R ²	R ³	R ⁴	I+II	I:II																																					
Me	H	Me	H	(6)	—																																					
Me	Me	Me	Me	(0)	—																																					
Ph	H	H	H	(30)	50:50																																					

TABLE II. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
C₃						
	$\begin{matrix} R^1 & R^2 \\ \hline H & COMe \\ H & 4-ClC_6H_4 \\ H & 4-(CN)C_6H_4 \\ H & Ph \\ H & CH_2CH_2PO(OEt)_2 \\ H & 4-MeC_6H_4 \\ H & 4-MeOC_6H_4 \end{matrix}$	$\begin{matrix} Cu(acac)_2 \\ Cu(F_6acac)_2 \\ Cu(F_6acac)_2 \\ Cu(F_6acac)_2 \\ CuSO_4 \\ Cu(F_6acac)_2 \\ Cu(F_6acac)_2 \end{matrix}$	$\begin{matrix} (10) \\ (45) \\ (33) \\ (57) \\ (17) \\ (60) \\ (66) \end{matrix}$	$\begin{matrix} 434 \\ 435 \\ 435 \\ 435 \\ 345 \\ 435 \\ 435 \end{matrix}$		
C₅	R					
	Me		$Cu(acac)_2$	(84)	41, 344	
	Me		$Cu(acac)_2$	(95)	41, 344	
C₇	Et	Br	$Rh_2(OAc)_4$	(75)	438	
C₁₁	<i>t</i> -Bu	Me	Cu powder	(—)	65	
	<i>t</i> -Bu	H	$Cu \cdot P(OMe)_3$	(87)	437	
C₁₅	<i>c</i> -C ₆ H ₁₁	H	CuOTf	(76)	436	
C₅	R = Me		$Cu(acac)_2$		(84)	41, 344
	R = Me		$Cu(acac)_2$		(95)	41, 344
R = Me		$Rh_2(OAc)_4$		(74)	439	
	$\begin{matrix} R^1 & R^2 \\ \hline H & H \\ Et & H \\ H & Me \end{matrix}$			(83)		
				(80)		
		$CuCl$		(12)	439	
R	R¹			(75-80)		
Me	H					
Me	Et					
R					439	
R		$Rh_2(OAc)_4, 20^\circ$		(54)		
Me		$CuCl, 80^\circ$		(28)	(35)	
Me						
R = Me		$Cu(acac)_2, 80^\circ C$		(68)	434	
	$\begin{matrix} n \\ 0 \\ 1 \end{matrix}$			(87)		

TABLE II. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Me		Cu(acac) ₂ , 80 °C	 I II III	434
	$\frac{R^1}{Me}$ Ph		$\frac{I \quad II \quad III}{(3) \quad (4) \quad (30)}$ (3) (10) (32)	
R = Me		Cu-bronze	(38)	440
R = Me		Cu-bronze	(70)	440
R = Me		1. Cu-bronze 2. MeOH/H ₂ O/HCl	(49)	440
R = Me	 $\frac{R^1}{H}$ Mc n-Bu	Rh ₂ (OAc) ₄	 (33) (79) (80)	441
R = Me		Cu(acac) ₂ Cu(F ₃ acac) ₂ Cu(F ₆ acac) ₂ Cu(Phacac) ₂ Cu(EtOacac) ₂ Cu(OTf) ₂ Rh ₂ (OAc) ₄	 (75) (5) (79) (—) (41) (52) (79) (—) (77) (—) (78) (—) (39) (12)	442, 361
R = Me		Cu CuCl CuSO ₄ CuCl•P(OMe) ₃ Cu(acac) ₂	 (38) (2) (43) (2) (45) (2) (63) (5) (78) (12)	61, 443, 140
R = Me		CuCl•P(OMe) ₃ , 110°	 (23) (2) (8) (20)	61

TABLE II. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Me		CuI•P(OMe) ₃	 (74) + (13)	61
R = Me		CuI•P(OMe) ₃	 (73)	61, 140
R = Me		CuI•P(OMe) ₃ , 98°	 (76)	443
R = Me		CuI•P(OMe) ₃ , 98°	 (96)	443
R = Me		CuI•P(OMe) ₃	 (80)	61, 140
R = Me		CuI•P(OMe) ₃	 (56)	68
C ₇	R = Et 	Cu powder, 100°	 (35)	444
C ₅	R = Me 	CuI•P(OMe) ₃	 (39)	68
R = Me R = <i>t</i> -Bu		Cu powder	 CO ₂ R ¹ CO ₂ Me R ¹ Me (65) <i>t</i> -Bu (60)	445
C ₁₁	R = <i>t</i> -Bu 	CuI•P(OMe) ₃	 (69)	437
C ₅	R = Me 	CuI•P(OMe) ₃	 (52)	437
R = Me		CuI•P(OMe) ₃	 (80)	61, 140
R = Me		CuI•P(OMe) ₃	 (85)	68
C ₁₁	R = <i>t</i> -Bu 	CuI•P(OMe) ₃	 (52)	437
C ₅	R = Me 	Rh ₂ (OAc) ₄	 (24)	446

TABLE II. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																
R = Me		Cu-bronze	(64)	447																																
$N_2=CH-CO_2R$		CuSO ₄	I + II + III (33-45) I:II:III = 66:29:5	448																																
C ₄ R = Me		CuSO ₄	(30-37)	448																																
C ₅ R = Et	 <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>OMe</td> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>OMe</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>OMe</td> </tr> <tr> <td>Et</td> <td>H</td> <td>Me</td> <td>Me</td> </tr> <tr> <td>Bu</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>Et</td> <td>OEt</td> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>H</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Me	OMe	H	H	Me	H	OMe	H	Me	H	H	OMe	Et	H	Me	Me	Bu	H	H	H	Et	OEt	Me	H	Me	Ph	H	H	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(58) (90) (82) (79) (62) (37) (64)	72
R ¹	R ²	R ³	R ⁴																																	
Me	OMe	H	H																																	
Me	H	OMe	H																																	
Me	H	H	OMe																																	
Et	H	Me	Me																																	
Bu	H	H	H																																	
Et	OEt	Me	H																																	
Me	Ph	H	H																																	
R = Et	 R ¹ = Et or Ph	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(36)	72																																
R = Et		Cu-bronze	(57)	130																																
R = Et		Cu-bronze Rh ₂ (OAc) ₄ Pd(PhCOCHCOMe) ₂ Cu(PhCOCHCOMe) ₂ CuCl•P(OMe) ₃ CuSO ₄	+ (—) (—) (76) (11) (51) (22) (53) (16) (48) (18) (60) (12)	130 135 135 135 135 135																																
R = Et	 R Me Et	Cu-bronze	(73) (52-70)	130																																
R = Et		Cu(acac) ₂	(low)	137																																

TABLE II. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		Cu(acac) ₂	 I + II (49) 75:25 (52) 75:25	137
R = Et		Cu(acac) ₂	 (low)	137
R = Et		Cu(acac) ₂	 (50)	72
C ₄		Cu(F ₆ acac) ₂	 (72) (67)	65
C ₅ C ₆				
C ₅ C ₆				
C ₅ C ₆				
C ₅ C ₆		Cu(F ₆ acac) ₂	 (76) (75)	65, 68
C ₅ C ₆				
C ₅ C ₆				
C ₅ C ₆				
C ₅		Cu(F ₆ acac) ₂	 (42) (6)	65
C ₅				
C ₅				
C ₅				
C ₆		Cu(F ₆ acac) ₂ Cu(acac) ₂	 I (16) II (4) III (6) IV (36) I (4) II (—) III (12) IV (—)	65
C ₅		Cu(F ₆ acac) ₂	 (25) (27)	65, 68
C ₅				
C ₅				
C ₅				
R = OMc		Cu(F ₆ acac) ₂	 (21)	65
C ₆				
C ₆		Cu(F ₆ acac) ₂	 (74)	65

TABLE II. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

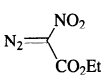

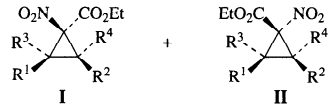
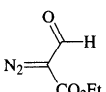

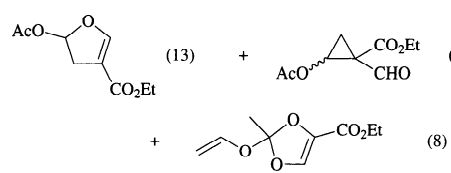

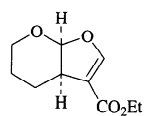
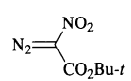

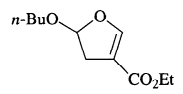

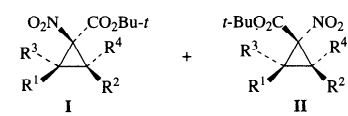
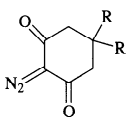

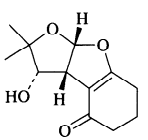
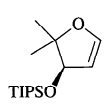
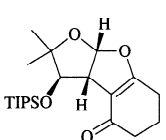
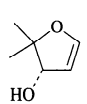
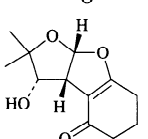

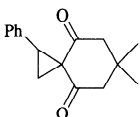
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				I+II	I:II																																							
			Me	(75)	—																																							
			Me	(65)	80:20																																							
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		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂		433																																								
			<table border="1"> <thead> <tr> <th></th> <th>I+II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(80)</td> <td>—</td> </tr> <tr> <td>Me</td> <td>(50)</td> <td>80:20</td> </tr> <tr> <td>—(CH₂)₄—</td> <td>(30)</td> <td>80:20</td> </tr> <tr> <td>Me</td> <td>(0)</td> <td>—</td> </tr> <tr> <td>Ph</td> <td>(83)</td> <td>67:33</td> </tr> </tbody> </table>		I+II	I:II	Me	(80)	—	Me	(50)	80:20	—(CH ₂) ₄ —	(30)	80:20	Me	(0)	—	Ph	(83)	67:33																							
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		1. Rh ₂ (OAc) ₄ 2. NaBH ₄		136																																								
	R = H		Rh ₂ (OAc) ₄		136																																							
	R = H		Rh ₂ (OAc) ₄		136																																							
	R = Me		Cu(acac) ₂		141																																							

TABLE II. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

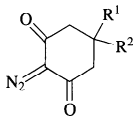
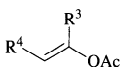
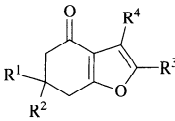
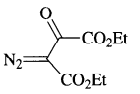

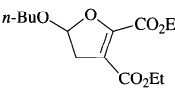
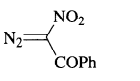
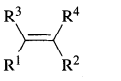

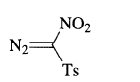
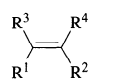

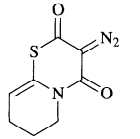

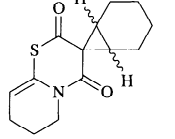
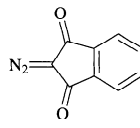

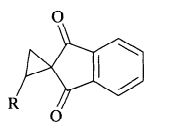

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
		1. Rh ₂ (OAc) ₄ 2. <i>p</i> -TsOH, toluene																																						
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>Me (<i>E</i> + <i>Z</i>)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	H	H	H	H	H	H	Me	H	Me	H	H	H	Me	H	H	Me (<i>E</i> + <i>Z</i>)	Me	Me	H	H	Me	Me	Me	H			(69) (62) (59) (41) (71) (64)	133, 134 134 134 134 134 134								
R ¹	R ²	R ³	R ⁴																																					
H	H	H	H																																					
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Me	H	H	Me (<i>E</i> + <i>Z</i>)																																					
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R ¹	R ²	R ³	R ⁴																																					
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		Rh ₂ (OAc) ₄		(97)																																				
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	<table border="1"> <thead> <tr> <th>R</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-C₈H₁₇</td> </tr> <tr> <td>Bn</td> </tr> </tbody> </table>	R	<i>n</i> -C ₈ H ₁₇	Bn		(72) (46)	450																																	
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<i>n</i> -C ₈ H ₁₇																																								
Bn																																								
		Rh ₂ (OAc) ₄																																						
			(41) (25)	450																																				

TABLE II. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING DIAZOACETOACETATES, DIAZOMALONATES, AND RELATED SYSTEMS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.														
		$\text{Rh}_2(\text{OAc})_4$	 (16)	450														
		$\text{Rh}_2(\text{OAc})_4$	 (46)	450														
		$\text{Rh}_2(\text{OAc})_4$	 (80-82) (52-53) (46-48) (63-72) (54-59) (0)	450														
	<table border="0"> <tr><td>R</td><td>_____</td></tr> <tr><td>Cl</td><td></td></tr> <tr><td>Br</td><td></td></tr> <tr><td>NO_2</td><td></td></tr> <tr><td>H</td><td></td></tr> <tr><td>Me</td><td></td></tr> <tr><td>OMe</td><td></td></tr> </table>	R	_____	Cl		Br		NO_2		H		Me		OMe				
R	_____																	
Cl																		
Br																		
NO_2																		
H																		
Me																		
OMe																		

TABLE III. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING VINYL AND PHENYL DIAZOACETATES

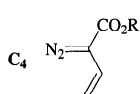

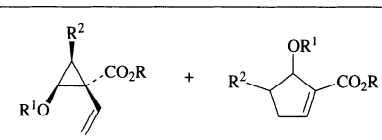

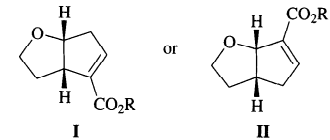
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R	R ¹	R ²																																									
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2,6- <i>(t</i> -Bu) ₂ -4-MeC ₆ H ₂	<i>n</i> -Bu	H																																									
2,6- <i>(t</i> -Bu) ₂ -4-MeC ₆ H ₂	Et	H																																									
2,6- <i>(t</i> -Bu) ₂ -4-MeC ₆ H ₂	Et	Me																																									
C ₄		Rh ₂ (OOct) ₄ , pentane	(91)	212																																							
C ₅		Rh ₂ (OOct) ₄ , pentane	(87)	212																																							
		Rh ₂ (OOct) ₄ , pentane	(76)	451, 143																																							
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(37)	143																																							
		Rh ₂ (OPfb) ₄ , CH ₂ Cl ₂	(0)	452, 143																																							
C ₈		Rh ₂ (OPiv) ₄ , pentane	(98)	451, 143																																							
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(33)	143																																							
		Rh ₂ (OPfb) ₄ , CH ₂ Cl ₂	(0)	144																																							
		Rh ₂ (OPiv) ₄ , pentane	(37)	451, 143																																							
C ₁₉		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(0)	143																																							
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(0)	143																																							
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(0)	452																																							
																																											
C ₅	R = Me	1. Rh ₂ (OOct) ₄ , pentane 2. Et ₂ AlCl, CH ₂ Cl ₂	I (66)	143																																							
C ₁₉	R = 2,6- <i>(t</i> -Bu) ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	II (42)	132																																							

TABLE III. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING VINYL AND PHENYL DIAZOACETOACETATES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ R = <i>t</i> -Bu		Rh ₂ (OOct) ₄ , pentane	 (74)	452
C ₁₉ R = 2,6-(<i>t</i> -Bu) ₂ -4-MeC ₆ H ₂		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	 (85)	451
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	 (44) + (25)	451
C ₄		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	 (15) + (58)	451
C ₆	R ¹ Me R ² Me		(15) (58)	
C ₉	R ¹ Me R ² <i>t</i> -Bu		(0) (0)	
C ₁₁	R ¹ Me R ² Ph		(0) (45)	
C ₁₁ R ¹ = Mc R ² = OTBDMS		Rh ₂ (OOct) ₄ , pentane	 (82)	144
			 I + II	
C ₆	R ¹ Me R ² Me R ³ OEt	Rh ₂ (OOct) ₄ , pentane	(68) >95:5	212
C ₁₁	R ¹ Me R ² Ph R ³ OEt	Rh ₂ (OPiv) ₄ , pentane	(75) >95:5	212
	R ¹ Me R ² Ph R ³ Ph	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(94) >95:5	59
C ₁₄	R ¹ Et R ² CH=CHPh R ³ Ph	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(94) >95:5	59
C ₁₁ R ¹ = Me R ² = Ph		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 16 h	 I + II	291
	R ³ TMS		(96) 93:7	
	R ³ TES		(93) >95:5	
	R ³ SiPh ₃		(81) >95:5	
C ₈ R ¹ = <i>t</i> -Bu R ² = H		Rh ₂ (OPiv) ₄ , pentane	 I + II (68) = I+II I:II = >95:5	452

TABLE III. DIASTERESELECTIVE CYCLOPROPANATION OF ALKENES USING VINYL AND PHENYL DIAZOACETATES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
			 I + II (56) >95:5 I:II (73) >95:5 I:II (66) >95:5	212
C ₅	R ¹ = Me R ² = H	Rh ₂ (OOct) ₄ , pentane		
C ₆	Me Me	Rh ₂ (OOct) ₄ , pentane		
C ₁₁	Me Ph	Rh ₂ (OPiv) ₄ , pentane		
	 R ¹ = Me R ² = Ph	Rh ₂ (OOct) ₄ , pentane	 (39)	212
	 R ¹ R ² R ³		 (83)	212
C ₆	Me H Me	Rh ₂ (OPiv) ₄ , pentane	(83)	212
C ₁₁	Me H Ph	Rh ₂ (OPiv) ₄ , pentane	(80)	212
C ₁₄	<i>t</i> -Bu OTBDMS H	Rh ₂ (OOct) ₄ , pentane	(82)	144
C ₉	 R	Catalyst, CH ₂ Cl ₂	 I + II (74) 90:10 I:II (44) 95:5 I:II (69) 98:2 I:II (96) 88:12 I:II (37) 97:3 I:II (61) 98:2 I:II (71) 98:2 I:II (70) 99:1	196 292 146 145 74 146 146 146
	R	Catalyst		
	CH ₂ N(TMS) ₂	Rh ₂ (OAc) ₄		
	OTMS	Rh ₂ (OAc) ₄		
	Ph	Rh ₂ (OAc) ₄		
	Ph	Rh ₂ (OAc) ₄		
	Ph	Rh ₂ (caprolactam) ₄		
	Ph	Rh ₂ (OPiv) ₄		
	Ph	Rh ₂ (TPA) ₄		
	Ph	Rh ₂ (TFA) ₄		
	 R	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	 I + II (70) 85:15 I:II (55) 76:24 I:II (79) >95:5 I:II (35) 92:8 I:II (72) 78:22 I:II (92) 85:15 I:II (96) 89:11 I:II (83) 84:16 I:II (68) 89:11 I:II (80) 95:5	59
	R			
	ClCH ₂			
	BrCH ₂			
	AcO			
	EtOCH ₂			
	<i>t</i> -Bu			
	<i>n</i> -Bu			
	Ph			
	<i>c</i> -C ₆ H ₁₁			
	Bn			
	4-(MeO)C ₆ H ₄			

TABLE III. DIASTEREOSELECTIVE CYCLOPROPANATION OF ALKENES USING VINYL AND PHENYL DIAZOACETATES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu powder	 (73) (76)	453
	$\frac{\text{R}}{n\text{-C}_5\text{H}_{11}}$ CH ₂ TMS			
		Cu powder	 (95)	453
C₁₁				
		Cu powder	 (54) + (4) + (-)	454

TABLE IV. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL AUXILIARIES (Continued)

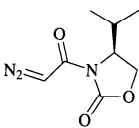

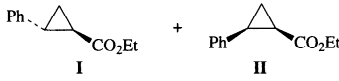
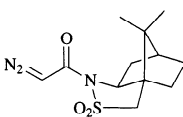
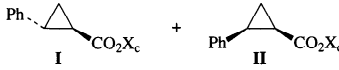
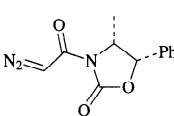
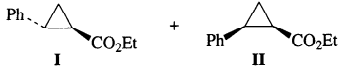
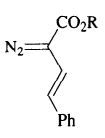

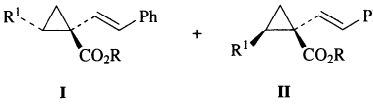

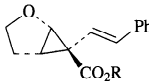

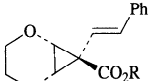
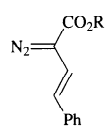
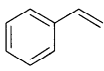
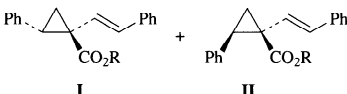
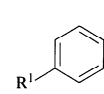
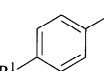
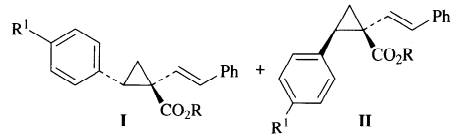
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																								
C₈ 		1. Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , reflux 2. EtONa, EtOH	 (20-24) I:II = 64:36 I ee = 13% (1 <i>R</i> ,2 <i>R</i>), II ee = —	110																																																																								
C₁₂ 		Catalyst (Chart 1), CH ₂ Cl ₂ , rt	 de (%) abs stereochem <table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(60)</td> <td>94:6</td> <td>57</td> <td>99</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(30)</td> <td>79:21</td> <td>35</td> <td>65</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(5)</td> <td>41:59</td> <td>28</td> <td>74</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(50)</td> <td>74:26</td> <td>80</td> <td>50</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> </tr> <tr> <td>(5)</td> <td>69:31</td> <td>54</td> <td>29</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> </tr> <tr> <td>(11)</td> <td>33:67</td> <td>82</td> <td>30</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> </tr> <tr> <td>(33)</td> <td>73:27</td> <td>63</td> <td>65</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(10)</td> <td>72:28</td> <td>67</td> <td>63</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(60)</td> <td>96:4</td> <td>54</td> <td>84</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(10)</td> <td>76:24</td> <td>47</td> <td>77</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(41)</td> <td>47:53</td> <td>25</td> <td>66</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> </tbody> </table>	I+II	I:II	I	II	I	II	(60)	94:6	57	99	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(30)	79:21	35	65	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(5)	41:59	28	74	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(50)	74:26	80	50	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	(5)	69:31	54	29	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	(11)	33:67	82	30	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	(33)	73:27	63	65	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(10)	72:28	67	63	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(60)	96:4	54	84	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(10)	76:24	47	77	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(41)	47:53	25	66	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	455
I+II	I:II	I	II	I	II																																																																							
(60)	94:6	57	99	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
(30)	79:21	35	65	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
(5)	41:59	28	74	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
(50)	74:26	80	50	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>																																																																							
(5)	69:31	54	29	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>																																																																							
(11)	33:67	82	30	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>																																																																							
(33)	73:27	63	65	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
(10)	72:28	67	63	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
(60)	96:4	54	84	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
(10)	76:24	47	77	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
(41)	47:53	25	66	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																							
C₁₃ 		1. Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 22° 2. EtONa, EtOH, 0°	 (35-40) I:II = 64:36 I ee = 14% (1 <i>R</i> ,2 <i>R</i>), II ee = 13% (1 <i>R</i> ,2 <i>S</i>)	110																																																																								
C₁₆  R = (<i>R</i>)-pantolactone		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 0°	 ee (%) abs stereochem <table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(71)</td> <td>>95:5</td> <td>92</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(42)</td> <td>>95:5</td> <td>90</td> <td>—</td> <td>—</td> <td>—</td> </tr> </tbody> </table>	I+II	I:II	I	II	I	II	(71)	>95:5	92	—	—	—	(42)	>95:5	90	—	—	—	148																																																						
I+II	I:II	I	II	I	II																																																																							
(71)	>95:5	92	—	—	—																																																																							
(42)	>95:5	90	—	—	—																																																																							
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 0°	 (86) 66% ee	148																																																																								
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 0°	 (65) 47% ee	148																																																																								

TABLE IV. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL AUXILIARIES (Continued)

Carbenoid Precursor		Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.	
			Catalyst, CH ₂ Cl ₂ , reflux								
						ee (%)		abs stereochem			
				I+II	I:II	I	II	I	II		
C ₁₂	<i>d</i> -menthyl		Rh ₂ (OAc) ₄	(81)	>95:5	3	—	—	—	147	
C ₁₄	(±)-5-OH-butyrolactone		Rh ₂ (OAc) ₄	(90)	>95:5	42	—	—	—	147, 148	
	(<i>S</i>)-methyl lactate		Rh ₂ (OAc) ₄	(83)	>95:5	67	—	1 <i>S</i> ,2 <i>S</i>	—	147, 148	
	(<i>S</i>)-methyl lactate		Rh ₂ (OPiv) ₄	(83)	>95:5	67	—	1 <i>S</i> ,2 <i>S</i>	—	147	
C ₁₅	(±)-3-OH-methyl butanoate		Rh ₂ (OAc) ₄	(77)	>95:5	12	—	—	—	148	
C ₁₆	(<i>R</i>)-pantolactone		Rh ₂ (OAc) ₄	(91)	>95:5	89	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>R</i>)-pantolactone		Rh ₂ (O ₂ CF ₃) ₄	(95)	>95:5	78	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>R</i>)-pantolactone		Rh ₂ [O(NH)CCH ₃] ₄	(37)	>95:5	76	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>R</i>)-pantolactone		Rh ₂ (OPiv) ₄	(95)	>95:5	69	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>R</i>)-pantolactone		Rh ₂ (OOct) ₄	(84)	>95:5	87	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>R</i>)-pantolactone		Rh ₂ (OOct) ₄ ^a	(84)	>95:5	97	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>R</i>)-pantolactone		Rh ₂ (O ₂ CH) ₄	(42)	>95:5	89	—	1 <i>R</i> ,2 <i>R</i>	—	148	
	(<i>R</i>)-pantolactone		Rh ₂ [(<i>S</i>)-O ₂ CCH(OH)(Ph)] ₄	(89)	>95:5	17	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>R</i>)-pantolactone		Rh ₂ [(<i>R</i>)-O ₂ CCH(OH)(Ph)] ₄	(95)	>95:5	81	—	1 <i>R</i> ,2 <i>R</i>	—	147, 148	
	(<i>S</i>)-2-OH-3-Me-methyl butanoate		Rh ₂ (OAc) ₄	(82)	>95:5	78	—	1 <i>S</i> ,2 <i>S</i>	—	148	
	C ₁₇	(<i>S</i>)-2-OH-3,3-Me ₂ -methyl butanoate		Rh ₂ (OAc) ₄	(81)	>95:5	79	—	1 <i>S</i> ,2 <i>S</i>	—	148
	C ₁₉	(±)-methyl mandelate		Rh ₂ (OAc) ₄	(71)	>95:5	59	—	—	—	147, 148
(±)-methyl mandelate			Rh ₂ (OPiv) ₄	(81)	>95:5	60	—	—	—	147	

Carbenoid Precursor		Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.
			Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 0°							
						ee (%)		abs stereochem		
				I+II	I:II	I	II	I	II	
	R ^I			(92)	>95:5	>95	—	—	—	148
	Cl			(75)	>95:5	>95	—	—	—	
	OMe									

^a This reaction was carried out at 0°.

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS

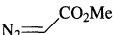

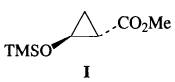
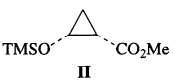

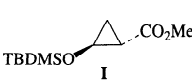
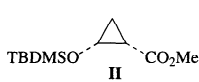

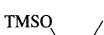
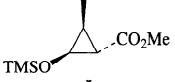
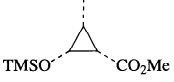

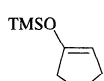
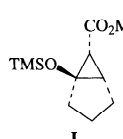
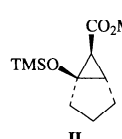

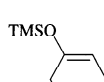
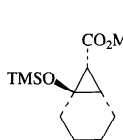
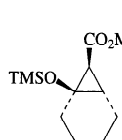
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																													
A. C₂-Symmetric Complexes (See Chart 2 for Catalyst Structures)																																																	
C₃																																																	
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TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)


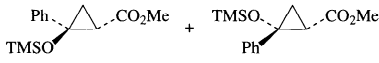
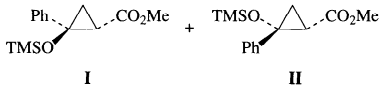
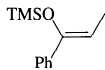
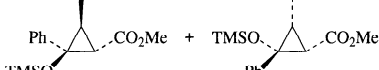
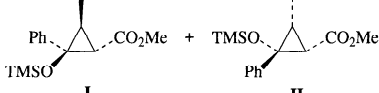
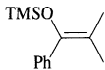

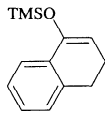
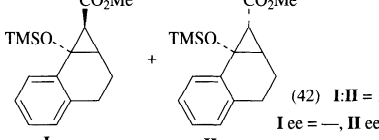
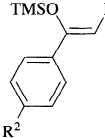
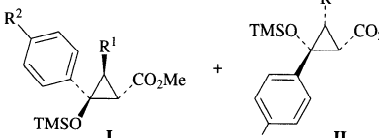
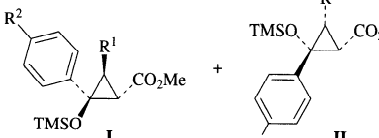
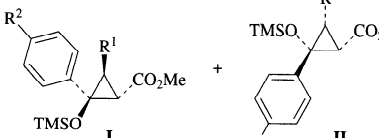
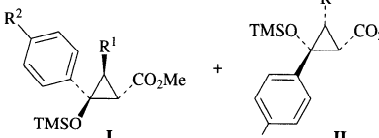
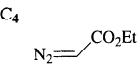

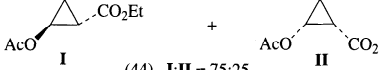

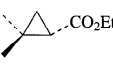
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																								
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		34b, DCE, rt, 5 h	 ee (%) abs stereochem <table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(37)</td> <td>30:70</td> <td>>95</td> <td>>95</td> <td>—</td> <td>—</td> </tr> <tr> <td>(40)</td> <td>43:57</td> <td>>95</td> <td>>95</td> <td>—</td> <td>—</td> </tr> <tr> <td>(49)</td> <td>84:16</td> <td>6</td> <td>24</td> <td>—</td> <td>—</td> </tr> <tr> <td>(37)</td> <td>85:15</td> <td>10</td> <td>20</td> <td>—</td> <td>—</td> </tr> <tr> <td>(27)</td> <td>87:13</td> <td>63</td> <td>42</td> <td>—</td> <td>—</td> </tr> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> </tbody> </table>				I+II	I:II	I	II	I	II	(0)	—	—	—	—	—	(0)	—	—	—	—	—	(37)	30:70	>95	>95	—	—	(40)	43:57	>95	>95	—	—	(49)	84:16	6	24	—	—	(37)	85:15	10	20	—	—	(27)	87:13	63	42	—	—	(0)	—	—	—	—	—	460															
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I+II	I:II	I	II	I	II																																																																							
(0)	—	—	—	—	—																																																																							
(0)	—	—	—	—	—																																																																							
(37)	30:70	>95	>95	—	—																																																																							
(40)	43:57	>95	>95	—	—																																																																							
(49)	84:16	6	24	—	—																																																																							
(37)	85:15	10	20	—	—																																																																							
(27)	87:13	63	42	—	—																																																																							
(0)	—	—	—	—	—																																																																							
		39a, CH ₂ Cl ₂ , 0° to rt, 24 h	 (44) I:II = 75:25 I ee = 64%, II ee = 60%	461																																																																								
					ent-34b, CHCl ₃ , 0° to rt, 19 h	 (91) ee = >99% (1S)	126																																																																					

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)



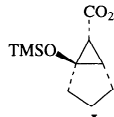
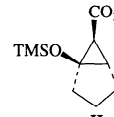


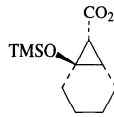
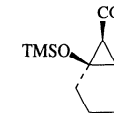
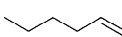
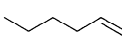
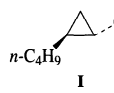
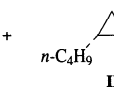
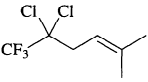
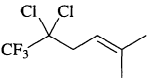
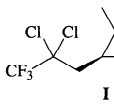
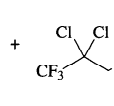
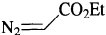

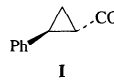
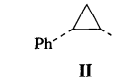
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.		
		Catalyst, CHCl ₃ , rt							459		
					ee (%)		abs stereochem				
				I+II	I:II	I	II	I		II	
			29a	(70)	27:73	56	56	1 <i>S</i> ,5 <i>R</i> ,6 <i>S</i>		1 <i>R</i> ,5 <i>S</i> ,6 <i>S</i>	
34b	(46)	25:75	40	85	1 <i>R</i> ,5 <i>S</i> ,6 <i>R</i>	1 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>					
85	(60)	35:65	0	0	—	—					
		29a, DCE, rt							459		
					(25) I:II = 33:67						
				I ee = —%, II ee = 72%							
		53b, AgOTf, CHCl ₃ , rt, 20 h							462		
					(42) I:II = 73:27						
				I ee = 76%, II ee = 83%							
		61, toluene, 80°							463		
					(—) I:II = 40:60						
				I ee = 0%, II ee = 26%							
											
					ee (%)		abs stereochem				
				I+II	I:II	I	II	I		II	
			28a, DCE, rt, 16 h	(65)	78:22	85	68	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	118, 69
			28b, DCE, rt, 5 h	(95)	63:37	24	14	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	464
			28b, DCE, 40°, 16 h	(60-80)	75:25	59	45	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	69, 118
			28c, DCE, 60°, 16 h	(60-80)	74:26	23	19	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	69, 118
			29a, CHCl ₃ , rt, 18 h	(80)	75:25	94	68	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	120
			29b, CHCl ₃ , rt, 18 h	(40)	75:25	66	43	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	120
			29c, CHCl ₃ , rt, 18 h	(45)	77:23	95	90	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	120
			30a, PhNHNH ₂ , DCE, rt, 24 h	(72)	71:29	46	31	1 <i>R</i> ,2 <i>R</i>		1 <i>S</i> ,2 <i>R</i>	124
			30b, PhNHNH ₂ , DCE, rt, 24 h	(80)	75:25	90	77	1 <i>R</i> ,2 <i>R</i>		1 <i>S</i> ,2 <i>R</i>	124
			30c, PhNHNH ₂ , DCE, rt, 24 h	(81)	70:30	60	52	1 <i>R</i> ,2 <i>R</i>		1 <i>S</i> ,2 <i>R</i>	124
			30d, PhNHNH ₂ , DCE, rt, 24 h	(76)	71:29	36	15	1 <i>R</i> ,2 <i>R</i>		1 <i>S</i> ,2 <i>R</i>	124
			31a, CH ₂ Cl ₂ , rt, 19 h	(—)	64:36	64	48	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	126
			31b, DCE, rt, 5 h	(60)	62:38	69	61	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	464
			ent-31b, CHCl ₃ , rt, 19 h	(—)	77:23	98	93	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	126
			31c, DCE, rt, 24 h	(81)	70:30	60	52	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	465
			32a, PhNHNH ₂ , DCE, rt, 24 h	(78)	71:29	28	30	1 <i>S</i> ,2 <i>S</i>		1 <i>R</i> ,2 <i>S</i>	124
			32b, PhNHNH ₂ , DCE, rt, 24 h	(88)	75:25	48	36	1 <i>S</i> ,2 <i>S</i>		1 <i>R</i> ,2 <i>S</i>	124
			32c, PhNHNH ₂ , DCE, rt, 24 h	(78)	72:28	19	31	1 <i>S</i> ,2 <i>S</i>		1 <i>R</i> ,2 <i>S</i>	124
			34a, CH ₂ Cl ₂ , 0° to rt, 19 h	(—)	69:31	49	45	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	126
			ent-34b, CH ₂ Cl ₂ , rt, 19 h	(77)	73:27	99	97	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	126
			34b, laponite, CH ₂ Cl ₂ , rt, 19 h	(39)	64:36	69	64	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	466
			ent-34c, DCE, rt, 5 h	(90)	70:30	40	42	1 <i>S</i> ,2 <i>S</i>		1 <i>S</i> ,2 <i>R</i>	464
			34c, laponite, CH ₂ Cl ₂ , 16 h	(44)	47:53	46	3	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	466, 467
			34d, EtNO ₂ , 23 h	(—)	64:36	45	40	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	467
			34d, laponite, CH ₂ Cl ₂ , rt, 40 h	(39)	55:45	31	26	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	466, 467
			34d, bentonite, CH ₂ Cl ₂ , rt, 23 h	(40)	58:42	34	21	1 <i>R</i> ,2 <i>R</i>		1 <i>R</i> ,2 <i>S</i>	466, 467

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

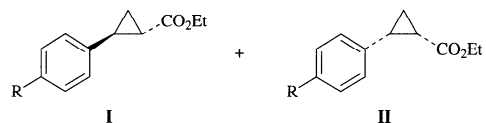
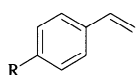
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
	34d , K10 montmorillonite, CH ₂ Cl ₂ , rt, 120 h	(11)	52:48	30	18	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	466
	35 , CHCl ₃ , rt, 19 h	(—)	66:34	3	8	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	126
	38 , CH ₂ Cl ₂ , 0° to rt, 24 h	(49)	64:36	59	30	— —	461, 468
	39a , CH ₂ Cl ₂ , 0° to rt, 24 h	(76)	70:30	84	65	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	461, 468
	39a , CHCl ₃ , 0° to rt, 24 h	(54)	67:33	73	—	1 <i>R</i> ,2 <i>R</i> —	461
	39a , neat, 0° to rt, 24 h	(48)	74:26	63	—	1 <i>R</i> ,2 <i>R</i> —	461
	39a , THF, 0° to rt, 24 h	(34)	80:20	37	—	1 <i>R</i> ,2 <i>R</i> —	461
	39a , toluene, 0° to rt, 24 h	(36)	78:22	59	—	1 <i>R</i> ,2 <i>R</i> —	461
	39a , pentane, 0° to rt, 24 h	(—)	—	—	—	— —	461
	39b , CH ₂ Cl ₂ , 0° to rt, 24 h	(78)	64:36	2	—	1 <i>R</i> ,2 <i>R</i> —	461, 468
	39c , —	(64)	80:20	38	21	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	469
	<i>ent</i> - 39c , —	(69)	79:21	49	34	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	469
	39d , CH ₂ Cl ₂ , 0° to rt, 24 h	(77)	68:32	50	39	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	461, 468
	39e , CH ₂ Cl ₂ , 0° to rt, 24 h	(80)	73:27	77	70	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	461
	40a , CH ₂ Cl ₂ , 0° to rt, 24 h	(77)	67:33	68	73	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	461
	40a , CH ₂ Cl ₂ , rt, 19 h	(64)	72:28	74	77	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	470
	40b , CH ₂ Cl ₂ , 0° to rt, 24 h	(85)	70:30	84	85	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	461
	40b , CH ₂ Cl ₂ , rt, 19 h	(56)	75:25	49	38	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	470
	41a , CH ₂ Cl ₂ , 0° to rt, 24 h	(53)	70:30	50	—	1 <i>R</i> ,2 <i>R</i> —	461
	41b , CH ₂ Cl ₂ , 0° to rt, 24 h	(71)	73:27	74	—	1 <i>R</i> ,2 <i>R</i> —	461
	41c , CH ₂ Cl ₂ , 0° to rt, 24 h	(60)	54:46	25	—	1 <i>R</i> ,2 <i>R</i> —	461
	41d , CH ₂ Cl ₂ , 0° to rt, 24 h	(59)	67:33	51	—	1 <i>R</i> ,2 <i>R</i> —	461
	41e , CH ₂ Cl ₂ , 0° to rt, 24 h	(50)	72:28	69	—	1 <i>R</i> ,2 <i>R</i> —	461
	41f , CH ₂ Cl ₂ , 0° to rt, 24 h	(26)	74:26	66	—	1 <i>R</i> ,2 <i>R</i> —	461
	42 , CH ₂ Cl ₂ , 0° to rt, 24 h	(58)	58:42	18	—	1 <i>S</i> ,2 <i>S</i> —	461
	43a , CH ₂ Cl ₂ , rt, 24 h	(72)	74:26	49	59	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	471
	43b , CH ₂ Cl ₂ , rt, 24 h	(69)	68:32	74	84	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	471
	44 , CH ₂ Cl ₂ , 0° to rt, 24 h	(12)	64:36	8	—	— —	461, 468
	45a , CHCl ₃ , rt, 20 h	(86)	64:36	26	0	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	472
	45b , CHCl ₃ , rt, 20 h	(93)	66:34	28	8	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	472
	46a , CHCl ₃ , rt, 6 h	(73)	63:37	40	41	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	473
	46a , CHCl ₃ , rt, 6 h	(58)	61:39	20	16	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	473
	46b , CHCl ₃ , rt, 6 h	(82)	66:34	15	12	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	473
	46b , CHCl ₃ , 0° to rt, 6 h	(63)	65:35	24	22	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	473
	47 , CHCl ₃ , rt, 6 h	(49)	64:36	48	50	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	473
	47 , CHCl ₃ , 0° to rt, 6 h	(77)	64:36	67	66	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	473
	50 , CH ₂ Cl ₂ , rt, 2 h	(50)	68:32	4	1	1 <i>R</i> ,2 <i>R</i> 1 <i>S</i> ,2 <i>R</i>	474
	51 , CH ₂ Cl ₂ , rt, 24 h	(5)	61:39	10	32	1 <i>R</i> ,2 <i>R</i> 1 <i>S</i> ,2 <i>R</i>	474
	52 , CH ₂ Cl ₂ , rt, 2 h	(60)	78:22	4	5	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	474
	53a , CHCl ₃ , rt, 5 h	(50)	80:20	89	74	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	462
	53b , AgOTf, CHCl ₃ , rt, 20 h	(48)	79:21	88	72	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	462
	53b , AgOTf, CHCl ₃ , 0°, 20 h	(52)	80:20	91	82	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	462
	54a , CHCl ₃ , rt, 5 h	(58)	60:40	62	61	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	475
	54b , CHCl ₃ , rt, 5 h	(59)	59:41	87	86	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	475
	54c , CHCl ₃ , rt, 5 h	(43)	67:33	55	57	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	475
	54d , CHCl ₃ , rt, 5 h	(59)	68:32	16	8	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	475
	55a , CHCl ₃ , rt, 5 h	(38)	64:36	4	4	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	475
	55b , CHCl ₃ , rt, 5 h	(52)	70:30	3	3	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	475
	<i>P-ent</i> - 56a , CHCl ₃ , rt, 4 h	(—)	69:31	14	18	— —	476
	<i>M</i> - 56b , CHCl ₃ , rt, 4 h	(—)	70:30	55	59	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	476
	<i>P</i> - 56b , CHCl ₃ , rt, 4 h	(—)	73:27	0	0	— —	476
	<i>M</i> - 56c , CHCl ₃ , rt, 4 h	(—)	78:22	49	53	— —	476
	<i>P</i> - 56c , CHCl ₃ , rt, 4 h	(—)	80:20	0	0	— —	476
	<i>M</i> - 56d , CHCl ₃ , rt, 4 h	(—)	65:35	33	34	— —	476
	<i>P</i> - 56d , CHCl ₃ , rt, 4 h	(—)	68:32	8	8	— —	476
	<i>M</i> - 56e , CHCl ₃ , rt, 4 h	(—)	67:33	34	13	— —	476
	<i>M</i> - 56f , CHCl ₃ , rt, 4 h	(—)	65:35	48	70	— —	476
	<i>P</i> - 56g , CHCl ₃ , rt, 4 h	(—)	70:30	66	70	— —	476

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

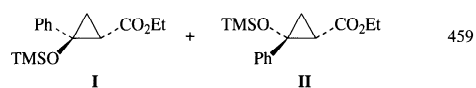
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.	
	<i>P</i> -56i, CHCl ₃ , rt, 4 h	(—)	67:33	88	89	—	—	476
	<i>P</i> -56j, CHCl ₃ , rt, 4 h	(—)	72:28	44	49	—	—	476
	<i>M</i> -56j, CHCl ₃ , rt, 4 h	(—)	90:10	0	10	—	—	476
	<i>M</i> -56k, CHCl ₃ , rt, 4 h	(—)	85:15	46	49	—	—	476
	57, CH ₂ Cl ₂ , rt	(21)	50:50	0	0	—	—	477
	58, CH ₂ Cl ₂ , rt	(76)	66:34	67	90	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	477
	59a, CHCl ₃ , 0° to rt, 24 h	(82)	75:25	60	52	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	478, 479, 480
	59b, CHCl ₃ , 0° to rt, 24 h	(43)	66:33	8	5	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	478
	59c, CHCl ₃ , 0° to rt, 24 h	(60)	75:25	58	—	1 <i>S</i> ,2 <i>S</i>	—	480
	59d, CHCl ₃ , 0° to rt, 24 h	(73)	75:25	90	—	1 <i>S</i> ,2 <i>S</i>	—	480
	60, CHCl ₃ , 0° to rt, 24 h	(60)	66:33	19	20	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	478
	62, —	(—)	—	<2	—	—	—	481
	63a, —	(—)	—	11	—	—	—	481
	63b, —	(—)	—	0	—	—	—	481
	63c, —	(—)	—	0	—	—	—	481
	64, —	(—)	—	11	—	—	—	481
	65, —	(—)	67:33	20	20	—	—	482
	66, PhNHNH ₂ , DCE, rt	(88)	74:26	86	58	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	483
	67a, —	(60)	67:33	12	2	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	484
	67b, —	(55)	74:26	9	24	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	484
	67c, —	(50)	73:27	8	5	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	484
	67d, —	(40)	65:35	2	10	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	484
	67e, —	(25)	68:32	3	9	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	484
	67f, —	(60)	71:29	8	40	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	484
	67g, —	(70)	78:22	20	36	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	484
	67h, —	(70)	75:25	12	25	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	484
	68a, —	(60)	71:29	4	2	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	484
	68b, —	(60)	74:26	4	5	1 <i>S</i> ,2 <i>S</i>	1 <i>R</i> ,2 <i>S</i>	484
	69, neat, 50°, 2 h	(8)	65:35	2	8	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	485
	70, neat, 50°, 2 h	(55)	70:30	18	58	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	485
	71, neat, 50°, 2 h	(60)	70:30	66	70	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	485
	72a, CH ₂ Cl ₂ , rt, 22 h	(75)	79:21	34	47	—	—	486
	73, neat, 80°	(—)	—	—	—	—	—	513
	74a, DCE, 45°, 18 h	(47)	66:34	1.7	27	1 <i>S</i> ,2 <i>S</i>	1 <i>R</i> ,2 <i>S</i>	487
	74b, DCE, rt, 18 h	(49)	67:33	40	73	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487
	74c, DCE, rt, 18 h	(58)	66:34	70	83	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487
	74d, DCE, rt, 18 h	(52)	61:39	62	74	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487
	75, CH ₂ Cl ₂ , rt	I (39)	76:24	73	44	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	488
	76a, —	(—)	—	—	—	—	—	489
	76b, —	(17)	—	5	—	1 <i>R</i> ,2 <i>R</i>	—	489
	76c, —	(—)	—	—	—	—	—	489
	77a, DCE, rt, 23 h	(70)	75:25	69	66	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	490
	77b, DCE, rt, 23 h	(69)	71:29	36	28	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	490
	77c, DCE, rt, 23 h	(91)	65:35	57	51	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	490
	77d, DCE, rt, 23 h	(85)	66:34	64	60	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	490
	77e, DCE, rt, 23 h	(85)	70:30	18	17	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	490
	77f, DCE, rt, 23 h	(83)	62:38	75	85	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	490
	78, —	(—)	—	37	—	—	—	489
	79a, DCE, rt, 23 h	(71)	60:40	32	30	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	491, 464
	79b, DCE, rt, 23 h	(78)	58:42	15	15	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	491
	80, DCE, rt, 23 h	(76)	61:39	7	5	1 <i>S</i> ,2 <i>S</i>	1 <i>R</i> ,2 <i>S</i>	491
	81, DCE, rt, 23 h	(71)	57:43	2	9	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	491
	82, DCE, rt, 23 h	(72)	62:38	8	14	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	491
	83, DCE, rt, 23 h	(62)	62:38	2	4	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	491
	84, DCE, -20°, 3 h	(—)	50:50	74	90	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	492
	87, CH ₂ Cl ₂ , 12 h	(40)	51:49	12	10	1 <i>S</i> ,2 <i>S</i>	1 <i>R</i> ,2 <i>S</i>	493
	88, CH ₂ Cl ₂ , 12 h	(42)	44:56	6	14	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	493
	89a, CH ₃ CN, PhNHNH ₂ , 50°	(41)	87:13	67	58	—	—	494

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

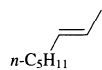
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.	
		89a , CH ₂ Cl ₂ , PhNHNH ₂ , 50°	(37)	90:10	38	35	—	494
		89a , DCE, PhNHNH ₂ , 50°	(37)	84:16	48	28	—	494
		89a , toluene, PhNHNH ₂ , 50°	(35)	88:12	54	50	—	494
		89b , CH ₃ CN, PhNHNH ₂ , 50°	(65)	71:29	81	92	—	494
		89c , CH ₃ CN, PhNHNH ₂ , 50°	(55)	73:27	86	92	—	494
		89c , CH ₂ Cl ₂ , PhNHNH ₂ , 50°	(—)	—	77	—	—	494
		89c , THF, PhNHNH ₂ , 50°	(—)	—	64	—	—	494
		89c , DCE, PhNHNH ₂ , 50°	(—)	—	83	—	—	494
		89c , DMF, PhNHNH ₂ , 50°	(—)	—	85	—	—	494
		89d , CH ₃ CN, PhNHNH ₂ , 50°	(64)	73:27	87	93	—	494
		89e , CH ₃ CN, PhNHNH ₂ , 50°	(59)	75:25	87	93	—	494



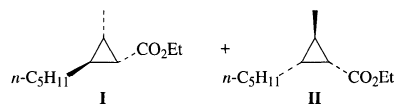
R	Conditions	ee (%)				abs stereochem		Refs.
		I+II	I:II	I	II	I	II	
Cl	53a , CHCl ₃ , rt, 20 h	(65)	83:17	87	83	—	—	462
Cl	53b , AgOTf, CHCl ₃ , rt, 20 h	(61)	84:16	89	84	—	—	462
Me	53a , CHCl ₃ , rt, 20 h	(72)	79:21	88	83	—	—	462
Me	53b , AgOTf, CHCl ₃ , rt, 20 h	(63)	80:20	88	83	—	—	462
OMe	53a , CHCl ₃ , rt, 20 h	(78)	75:25	77	63	—	—	462
OMe	53b , AgOTf, CHCl ₃ , rt, 20 h	(60)	75:25	77	63	—	—	462
<i>t</i> -Bu	28b , DCE, rt, 5 h	(76)	65:35	42	28	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	464
<i>t</i> -Bu	31b , DCE, rt, 5 h	(87)	66:34	80	66	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	464
<i>t</i> -Bu	79a , DCE, rt, 5 h	(71)	60:40	32	30	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	464



	Conditions	ee (%)				abs stereochem		Refs.
		I+II	I:II	I	II	I	II	
	29a , DCE, rt	(81)	68:32	77	77	—	—	459
	34b , CHCl ₃ , rt	(77)	56:44	90	95	—	—	459



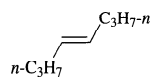
48d, CH₂Cl₂, rt, 2 h



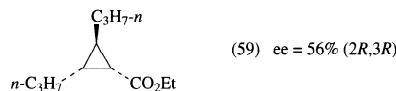
(64) I:II = 48:52

I ee = 72%, II ee = 75%

495



48d, CH₂Cl₂, rt, 2 h

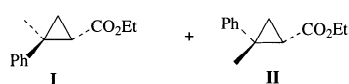


(59) ee = 56% (2*R*,3*R*)

495



66, PhNHNH₂, DCE, rt



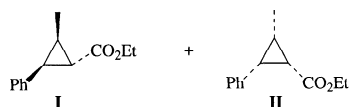
(98) I:II = 58:42

I ee = 84% (1*S*), II ee = 74% (1*S*)

483



53b, AgOTf, CHCl₃, rt, 20 h



(60) I:II = 96:4

I ee = 47%, II ee = 32%

462

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																																																																													
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I:II	I	II	I	II	II																																																																																																																																																												
29a, DCE, rt	(39)	I:II = 32:68	I ee = —%	II ee = 65%	—	459																																																																																																																																																											
			 <table border="1"> <thead> <tr> <th colspan="2">I+II</th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> <th rowspan="2">Refs.</th> </tr> <tr> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>28a, DCE, rt, 16 h</td> <td>(60)</td> <td>84:16</td> <td>93</td> <td>92</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> <td>118, 69</td> </tr> <tr> <td>29a, CHCl₃, rt, 18 h</td> <td>(87)</td> <td>86:14</td> <td>96</td> <td>90</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> <td>120</td> </tr> <tr> <td>29c, DCE, rt, 18 h</td> <td>(75)</td> <td>81:19</td> <td>94</td> <td>95</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> <td>120</td> </tr> <tr> <td>30b, PhNHNH₂, DCE, rt, 24 h</td> <td>(73)</td> <td>80:20</td> <td>94</td> <td>89</td> <td>—</td> <td>—</td> <td>124</td> </tr> <tr> <td>34b, CH₂Cl₂, rt, 19 h</td> <td>(75)</td> <td>81:19</td> <td>96</td> <td>93</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>126</td> </tr> <tr> <td>39a, CH₂Cl₂, rt, 24 h</td> <td>(84)</td> <td>82:18</td> <td>88</td> <td>84</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>461, 468</td> </tr> <tr> <td>40a, CH₂Cl₂, rt</td> <td>(48)</td> <td>84:16</td> <td>80</td> <td>17</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>470</td> </tr> <tr> <td>40b, CH₂Cl₂, rt</td> <td>(75)</td> <td>66:34</td> <td>36</td> <td>7</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>470</td> </tr> <tr> <td>40c, CH₂Cl₂, rt</td> <td>(75)</td> <td>88:12</td> <td>52</td> <td>15</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>470</td> </tr> <tr> <td>40d, CH₂Cl₂, rt</td> <td>(85)</td> <td>70:30</td> <td>84</td> <td>85</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>470</td> </tr> <tr> <td>45a, CHCl₃, rt, 20 h</td> <td>(95)</td> <td>70:30</td> <td>33</td> <td>0</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>472</td> </tr> <tr> <td>45b, CHCl₃, rt, 20 h</td> <td>(80)</td> <td>70:30</td> <td>35</td> <td>6</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>472</td> </tr> <tr> <td>ent-48a, CH₂Cl₂, rt, 2 h</td> <td>(72)</td> <td>72:28</td> <td>77</td> <td>73</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> <td>497</td> </tr> <tr> <td>48b, CH₂Cl₂, rt, 2 h</td> <td>(64)</td> <td>75:25</td> <td>77</td> <td>—</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> <td>498</td> </tr> <tr> <td>48c, CH₂Cl₂, rt, 2 h</td> <td>(53)</td> <td>66:34</td> <td>83</td> <td>—</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> <td>498, 499</td> </tr> <tr> <td>48d, CH₂Cl₂, rt, 2 h</td> <td>(75)</td> <td>86:14</td> <td>92</td> <td>98</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> <td>498, 499</td> </tr> <tr> <td>48e, CH₂Cl₂, rt, 2 h</td> <td>(75)</td> <td>57:43</td> <td>66</td> <td>—</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> <td>498</td> </tr> <tr> <td>48f, CH₂Cl₂</td> <td>(85)</td> <td>81:19</td> <td>92</td> <td>—</td> <td>—</td> <td>—</td> <td>499</td> </tr> </tbody> </table>	I+II		ee (%)		abs stereochem		Refs.	I:II	I	II	I	II	II	28a, DCE, rt, 16 h	(60)	84:16	93	92	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	118, 69	29a, CHCl ₃ , rt, 18 h	(87)	86:14	96	90	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	120	29c, DCE, rt, 18 h	(75)	81:19	94	95	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	120	30b, PhNHNH ₂ , DCE, rt, 24 h	(73)	80:20	94	89	—	—	124	34b, CH ₂ Cl ₂ , rt, 19 h	(75)	81:19	96	93	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	126	39a, CH ₂ Cl ₂ , rt, 24 h	(84)	82:18	88	84	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	461, 468	40a, CH ₂ Cl ₂ , rt	(48)	84:16	80	17	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470	40b, CH ₂ Cl ₂ , rt	(75)	66:34	36	7	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470	40c, CH ₂ Cl ₂ , rt	(75)	88:12	52	15	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470	40d, CH ₂ Cl ₂ , rt	(85)	70:30	84	85	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470	45a, CHCl ₃ , rt, 20 h	(95)	70:30	33	0	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	472	45b, CHCl ₃ , rt, 20 h	(80)	70:30	35	6	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	472	ent-48a, CH ₂ Cl ₂ , rt, 2 h	(72)	72:28	77	73	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	497	48b, CH ₂ Cl ₂ , rt, 2 h	(64)	75:25	77	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498	48c, CH ₂ Cl ₂ , rt, 2 h	(53)	66:34	83	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498, 499	48d, CH ₂ Cl ₂ , rt, 2 h	(75)	86:14	92	98	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498, 499	48e, CH ₂ Cl ₂ , rt, 2 h	(75)	57:43	66	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498	48f, CH ₂ Cl ₂	(85)	81:19	92	—	—	—	499	
I+II		ee (%)		abs stereochem		Refs.																																																																																																																																																											
I:II	I	II	I	II	II																																																																																																																																																												
28a, DCE, rt, 16 h	(60)	84:16	93	92	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	118, 69																																																																																																																																																										
29a, CHCl ₃ , rt, 18 h	(87)	86:14	96	90	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	120																																																																																																																																																										
29c, DCE, rt, 18 h	(75)	81:19	94	95	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	120																																																																																																																																																										
30b, PhNHNH ₂ , DCE, rt, 24 h	(73)	80:20	94	89	—	—	124																																																																																																																																																										
34b, CH ₂ Cl ₂ , rt, 19 h	(75)	81:19	96	93	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	126																																																																																																																																																										
39a, CH ₂ Cl ₂ , rt, 24 h	(84)	82:18	88	84	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	461, 468																																																																																																																																																										
40a, CH ₂ Cl ₂ , rt	(48)	84:16	80	17	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470																																																																																																																																																										
40b, CH ₂ Cl ₂ , rt	(75)	66:34	36	7	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470																																																																																																																																																										
40c, CH ₂ Cl ₂ , rt	(75)	88:12	52	15	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470																																																																																																																																																										
40d, CH ₂ Cl ₂ , rt	(85)	70:30	84	85	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	470																																																																																																																																																										
45a, CHCl ₃ , rt, 20 h	(95)	70:30	33	0	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	472																																																																																																																																																										
45b, CHCl ₃ , rt, 20 h	(80)	70:30	35	6	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	472																																																																																																																																																										
ent-48a, CH ₂ Cl ₂ , rt, 2 h	(72)	72:28	77	73	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	497																																																																																																																																																										
48b, CH ₂ Cl ₂ , rt, 2 h	(64)	75:25	77	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498																																																																																																																																																										
48c, CH ₂ Cl ₂ , rt, 2 h	(53)	66:34	83	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498, 499																																																																																																																																																										
48d, CH ₂ Cl ₂ , rt, 2 h	(75)	86:14	92	98	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498, 499																																																																																																																																																										
48e, CH ₂ Cl ₂ , rt, 2 h	(75)	57:43	66	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	498																																																																																																																																																										
48f, CH ₂ Cl ₂	(85)	81:19	92	—	—	—	499																																																																																																																																																										

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.																														
	49a, CH ₂ Cl ₂ , rt, 2 h		(81)	69:31	72	67	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	497																														
	ent-49b, CH ₂ Cl ₂		(76)	81:19	94	—	—	—	499																														
	53a, CHCl ₃ , rt, 20 h		(75)	90:10	92	71	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	462																														
	54a, CHCl ₃ , rt, 5 h		(48)	72:28	72	71	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	475																														
	54b, CHCl ₃ , rt, 5 h		(67)	72:28	89	92	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	475																														
	66, PhNHNH ₂ , DCE, rt		(55)	83:17	72	—	1 <i>S</i> ,2 <i>S</i>	—	483																														
	72a, CH ₂ Cl ₂ , rt, 22 h		(77)	81:19	50	28	—	—	486																														
	74b, DCE, rt, 18 h		(31)	73:27	37	62	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487																														
	74c, DCE, rt, 18 h		(36)	74:26	73	90	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487																														
	75, CH ₂ Cl ₂ , rt		I (63)	86:14	87	82	—	—	488																														
	48d, CH ₂ Cl ₂ , rt, 2 h								498																														
			<table border="1"> <thead> <tr> <th colspan="2"></th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(72)</td> <td>82:18</td> <td>95</td> <td>98</td> <td>—</td> <td>—</td> </tr> <tr> <td>(73)</td> <td>90:10</td> <td>83</td> <td>>99</td> <td>—</td> <td>—</td> </tr> </tbody> </table>								ee (%)		abs stereochem		I+II	I:II	I	II	I	II	(72)	82:18	95	98	—	—	(73)	90:10	83	>99	—	—							
		ee (%)		abs stereochem																																			
I+II	I:II	I	II	I	II																																		
(72)	82:18	95	98	—	—																																		
(73)	90:10	83	>99	—	—																																		
	29a, DCE, rt								459																														
			(82) I:II = 65:35 I ee = 70%, II ee = 60%																																				
	48d, CH ₂ Cl ₂ , rt, 2 h								498																														
			(65) I:II = 85:15 I ee = 91%, II ee = —																																				
	48d, CH ₂ Cl ₂ , rt, 2 h								495																														
			(67) I:II = 50:50 I ee = 69%, II ee = 75%																																				
	48d, CH ₂ Cl ₂ , rt, 2 h								495																														
			(55) ee = 53% (2 <i>R</i> , 3 <i>R</i>)																																				
	Catalyst, CH ₂ Cl ₂ , rt, 2 h																																						
			<table border="1"> <thead> <tr> <th colspan="2"></th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(45)</td> <td>49:51</td> <td>2</td> <td>81</td> <td>1<i>S</i>,2<i>R</i>,3<i>S</i></td> <td>1<i>S</i>,2<i>S</i>,3<i>R</i></td> </tr> <tr> <td>(54)</td> <td>40:60</td> <td>24</td> <td>>99</td> <td>1<i>S</i>,2<i>R</i>,3<i>S</i></td> <td>1<i>S</i>,2<i>S</i>,3<i>R</i></td> </tr> <tr> <td>(62)</td> <td>66:34</td> <td>33</td> <td>74</td> <td>1<i>S</i>,2<i>R</i>,3<i>S</i></td> <td>1<i>S</i>,2<i>S</i>,3<i>R</i></td> </tr> </tbody> </table>								ee (%)		abs stereochem		I+II	I:II	I	II	I	II	(45)	49:51	2	81	1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i>	1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>	(54)	40:60	24	>99	1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i>	1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>	(62)	66:34	33	74	1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i>	1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>	495, 498, 495
		ee (%)		abs stereochem																																			
I+II	I:II	I	II	I	II																																		
(45)	49:51	2	81	1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i>	1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>																																		
(54)	40:60	24	>99	1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i>	1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>																																		
(62)	66:34	33	74	1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i>	1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>																																		
	48d, CH ₂ Cl ₂ , rt, 2 h								498																														
			(94) I:II = >99:1 I ee = 73%, II ee = —																																				
	48d, CH ₂ Cl ₂ , rt, 2 h								495																														
			(45) I:II = 45:55 I ee = 35% (1 <i>S</i> ,2 <i>R</i> ,3 <i>S</i>), II ee = >99% (1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>)																																				

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		48b , DCE, rt, 1 h	 (30) I:II = 79:21 I ee = 19%, II ee = 51%	458
		39a , CH ₂ Cl ₂ , 0°, 21 h 53a , CHCl ₃ , rt, 20 h	 ee (%) abs stereochem (90) 92 — (56) 87 —	461, 468 462
C₉		34b , CHCl ₃	 (54) I:II = 99:1 I ee = 8%	74
		66 , DCE, PhNHNH ₂ , rt	 (77) I:II = 89:11 I ee = 86% (1 <i>S</i> ,2 <i>S</i>)	483
C₁₀		34b , CHCl ₃ , rt	 (68) I:II = 86:14 Ar = 2,6-Me ₂ C ₆ H ₃ I ee = 97% (1 <i>R</i> ,2 <i>R</i>), II ee = 96% (1 <i>R</i> ,2 <i>S</i>)	126
C₁₁		ent-34c , pentane, rt 34b , pentane, 0°	 ee (%) abs stereochem (62) 65 — (23) 3 —	500
		39a , CH ₂ Cl ₂ , 0°, 21 h 40b , CH ₂ Cl ₂ , 0°, 21 h	 ee (%) abs stereochem I+II I:II I II I II (64) 72:28 74 88 — — (51) 72:28 62 80 — —	461
		31d , PhNHNH ₂ , CH ₂ Cl ₂ , rt 72a , CH ₂ Cl ₂ , rt, 22 h 72a , CH ₂ Cl ₂ , -20°, 22 h	 ee (%) abs stereochem (63) 95 1 <i>R</i> (66) 65 — (60) 58 —	496 486 486
		72a , CH ₂ Cl ₂ , rt, 22 h	(90) ee = 57%	486
		28a , DCE, rt	 (25-30) I:II = 82:18 I ee = 92% (1 <i>S</i> ,2 <i>S</i>), II ee = 92% (1 <i>S</i> ,2 <i>R</i>)	118, 69

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)


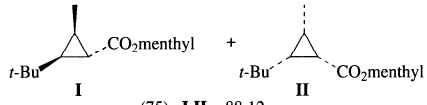

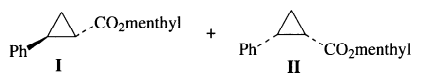
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.				
<i>l</i> -menthyl		36a , CH ₂ Cl ₂ , 0°, 14 h	 I + II = 88:12 I ee = 95%, II ee = 80%		125				
			 I + II = 88:12 I ee = 95%, II ee = 80%						
Menthyl stereochemistry			ee (%)		abs stereochem				
			I:II	I:II	I	II			
<i>d</i>		28a , DCE, rt, 16 h	(60-70)	82:18	97	95	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	118, 69
<i>l</i>		28a , DCE, rt, 16 h	(65-75)	85:15	91	90	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	118, 69
<i>d</i>		29a , DCE, rt	(89)	84:16	98	99	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	120
<i>d</i>		29c , DCE, rt	(75)	84:16	98	99	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	120
<i>d</i>		30b , PhNHNH ₂ , DCE, rt	(71)	84:16	98	80	—	—	124
<i>l</i>		30b , PhNHNH ₂ , DCE, rt	(77)	86:14	98	96	—	—	124
<i>l</i>		31a , DCE, rt	(60-80)	84:16	13	5	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	121
<i>l</i>		31b , DCE, rt	(60-80)	86:14	19	5	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	121
<i>l</i>		31b , PhNHNH ₂ , DCE, rt	(60-80)	87:13	96	97	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	121
<i>l</i>		31c , DCE, rt	(60-80)	83:17	55	50	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	121
<i>l</i>		31d , DCE, rt	(60-80)	86:14	19	9	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	121
<i>d</i>		<i>ent</i> - 31e , DCE, rt	(60-80)	83:17	90	90	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	121
<i>d</i>		<i>ent</i> - 31e , PhNHNH ₂ , DCE, rt	(60-80)	83:17	78	71	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	121
<i>l</i>		31f , DCE, rt	(60-80)	85:15	9	9	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	121
<i>l</i>		<i>ent</i> - 33 , DCE, rt	(60-80)	82:18	34	56	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	121
<i>l</i>		39a , CH ₂ Cl ₂ , 0°, 24 h	(86)	85:15	89	89	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	461, 468
<i>l</i>		43a , CH ₂ Cl ₂ , rt, 24 h	(60)	79:21	70	87	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	471
<i>l</i>		43b , CH ₂ Cl ₂ , rt, 24 h	(60)	81:19	84	92	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	471
<i>d</i>		54a , CHCl ₃ , rt, 5 h	(51)	84:16	75	52	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	475
<i>l</i>		54a , CHCl ₃ , rt, 5 h	(50)	68:32	87	91	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	475
<i>d</i>		54b , CHCl ₃ , rt, 5 h	(68)	86:14	90	87	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	475
<i>l</i>		54b , CHCl ₃ , rt, 5 h	(60)	68:32	95	97	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	475
<i>d</i>		66 , PhNHNH ₂ , DCE, rt	(55)	90:10	88	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	483
<i>l</i>		66 , PhNHNH ₂ , DCE, rt	(86)	91:9	94	—	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	483
<i>l</i>		66 , PhNHNH ₂ , DCE, 0°	(50)	93:7	96	66	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	483
<i>d</i>		<i>ent</i> - 70 , neat, 50°, 3 h	(68)	89:11	38	11	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	485
<i>l</i>		<i>ent</i> - 70 , neat, 50°, 3 h	(67)	82:18	76	79	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	485
<i>l</i>		72a , CH ₂ Cl ₂ , rt, 22 h	(81)	83:17	57	43	—	—	486
<i>l</i>		72a , CH ₂ Cl ₂ , 0°, 22 h	(92)	85:15	55	63	—	—	486
<i>l</i>		<i>ent</i> - 72a , CH ₂ Cl ₂ , rt, 22 h	(96)	82:18	57	85	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	486
<i>l</i>		72b , CH ₂ Cl ₂ , rt, 22 h	(85)	75:25	39	6	—	—	486
<i>l</i>		72c , CH ₂ Cl ₂ , rt, 22 h	(95)	81:19	50	41	—	—	486
<i>l</i>		72d , CH ₂ Cl ₂ , rt, 22 h	(84)	69:31	15	6	—	—	486
<i>l</i>		72e , CH ₂ Cl ₂ , rt, 22 h	(87)	73:27	36	9	—	—	486
<i>l</i>		72f , CH ₂ Cl ₂ , rt, 22 h	(89)	71:29	37	25	—	—	486
<i>d</i>		74b , DCE, rt, 18 h	(56)	87:13	59	49	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487
<i>l</i>		74b , DCE, rt, 18 h	(63)	81:19	73	84	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487
<i>d</i>		74c , DCE, rt, 18 h	(63)	88:12	87	86	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487
<i>l</i>		74c , DCE, rt, 18 h	(64)	77:23	90	99	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	487
<i>d</i>		75 , CH ₂ Cl ₂ , rt	I (67)	88:12	87	81	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	488
<i>l</i>		75 , CH ₂ Cl ₂ , rt	I (66)	85:15	89	84	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	488
<i>d</i>		79 , DCE, rt, 23 h	(73)	76:24	5	23	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	491
<i>l</i>		79 , DCE, rt, 23 h	(74)	78:22	30	34	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	491
<i>d</i>		82 , DCE, rt, 23 h	(74)	82:18	8	10	1 <i>S</i> ,2 <i>S</i>	1 <i>R</i> ,2 <i>S</i>	491

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Menthyl stereochemistry <i>d</i> <i>l</i>		30b , PhNHNH ₂ , DCE, rt, 24 h	 I + II ee (%) I:II I II (55) 98:2 77 — — — (60) 95:5 80 91 — —	124
			R = menthyl	
Menthyl stereochemistry <i>d</i> <i>l</i>		30b , PhNHNH ₂ , DCE, rt, 24 h	 I + II ee (%) I:II I II (72) 90:10 75 45 — — (76) 94:6 99 30 — —	124
			R = menthyl	
Menthyl stereochemistry <i>d</i> <i>l</i>		30b , PhNHNH ₂ , DCE, rt, 24 h	 I ee (%) (50) 85 — (52) 88 —	124
			R = menthyl	
<i>l</i> -menthyl		36a , CH ₂ Cl ₂ , 0°, 14 h	 I + II (54) I:II = 86:14 I ee = 82%	125
Menthyl stereochemistry <i>d</i> <i>l</i> <i>l</i> <i>l</i>		30b , PhNHNH ₂ , DCE, rt, 24 h	 I + II ee (%) I:II I II (72) 85:15 83 77 — — (78) 89:11 92 79 — — (70) 57:43 85 63 — — (96) 72:28 61 78 — —	124
		30b , PhNHNH ₂ , DCE, rt, 24 h		
		39a , CH ₂ Cl ₂ , 0°, 21 h		
		72a , CH ₂ Cl ₂ , rt, 22 h		
<i>l</i> -menthyl		36a , CH ₂ Cl ₂ , 0°, 14 h	 I + II (72) I:II = 88:12 I ee = 92%, II ee = 76%	125
<i>l</i> -menthyl		34b , DCE, rt, 1 h	 I + II (69) I:II = 78:22 I ee = 9%, II ee = 62%	458
<i>l</i> -menthyl		72a , CH ₂ Cl ₂ , rt, 22 h	 I + II (90) I:II = 90:10 I ee = 76%, II ee = 62%	486

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)


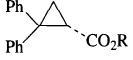
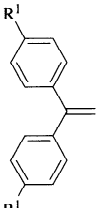
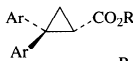
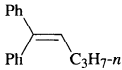
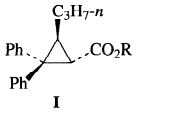
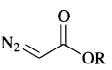
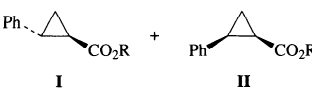
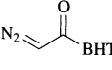
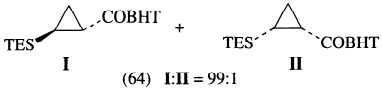

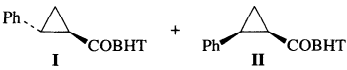
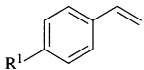
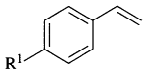
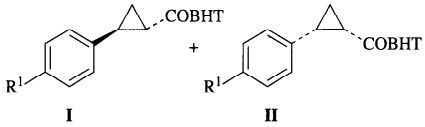

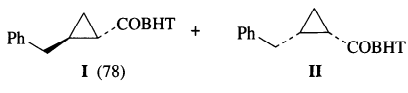
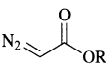
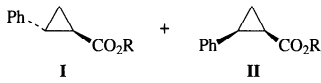

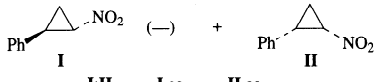
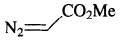
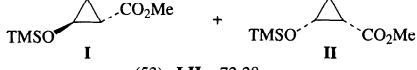
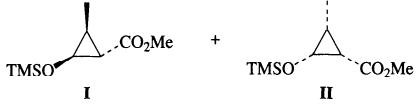
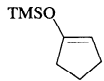
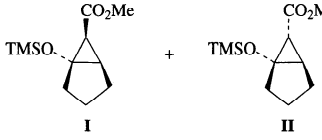
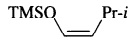
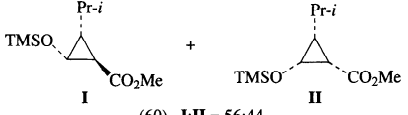
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
Menthyl stereochemistry		 R = menthyl	<table border="1"> <thead> <tr> <th>ee (%)</th> <th>abs stereochem</th> </tr> </thead> <tbody> <tr> <td>(58)</td> <td>1R</td> </tr> <tr> <td>(69)</td> <td>1S</td> </tr> <tr> <td>(75)</td> <td>1S</td> </tr> <tr> <td>(80)</td> <td>1S</td> </tr> <tr> <td>(83)</td> <td>1S</td> </tr> <tr> <td>(80)</td> <td>1S</td> </tr> <tr> <td>(71)</td> <td>1S</td> </tr> </tbody> </table>	ee (%)	abs stereochem	(58)	1R	(69)	1S	(75)	1S	(80)	1S	(83)	1S	(80)	1S	(71)	1S	496		
			ee (%)	abs stereochem																		
			(58)	1R																		
			(69)	1S																		
			(75)	1S																		
			(80)	1S																		
			(83)	1S																		
(80)	1S																					
(71)	1S																					
<i>l</i>	31d , PhNHNH ₂ , CH ₂ Cl ₂ , rt	(58)	82	1R	496																	
<i>l</i>	72a , CH ₂ Cl ₂ , rt, 22 h	(69)	74	1S	486																	
<i>l</i>	72a , CH ₂ Cl ₂ , 0°, 22 h	(75)	90	1S	486																	
<i>l</i>	72a , CH ₂ Cl ₂ , -20°, 22 h	(80)	95	1S	486																	
<i>l</i>	72a , CH ₂ Cl ₂ , -40°, 22 h	(83)	98	1S	486																	
<i>l</i>	72a •Cu(MeCN) ₄ PF ₆ , CH ₂ Cl ₂ , rt, 22 h	(80)	93	1S	486																	
<i>l</i>	72a •Cu(MeCN) ₄ PF ₆ , CH ₂ Cl ₂ , -20°, 22 h	(71)	96	1S	486																	
Menthyl stereochemistry	 R ¹	 R = menthyl Ar = 4-R ¹ C ₆ H ₄	<table border="1"> <thead> <tr> <th>ee (%)</th> <th>abs stereochem</th> </tr> </thead> <tbody> <tr> <td>(82)</td> <td>—</td> </tr> <tr> <td>(43)</td> <td>—</td> </tr> </tbody> </table>	ee (%)	abs stereochem	(82)	—	(43)	—	486												
			ee (%)	abs stereochem																		
			(82)	—																		
(43)	—																					
<i>l</i>	72a , CH ₂ Cl ₂ , rt, 22 h	(82)	96	—	486																	
<i>l</i>	R ¹ = Cl	(43)	94	—	486																	
<i>l</i> -menthyl	 C ₃ H _{7-n}	 I + II R = menthyl	<table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(52)</td> <td>98:2</td> <td>—</td> <td>—</td> </tr> <tr> <td colspan="4">I ee = 84%</td> </tr> </tbody> </table>	I+II	I:II	I	II	(52)	98:2	—	—	I ee = 84%				125						
			I+II	I:II	I	II																
(52)	98:2	—	—																			
I ee = 84%																						
<i>l</i>	36a , CH ₂ Cl ₂ , 0°, 14 h	(52)	I:II = 98:2	I ee = 84%	125																	
C ₁₅	 R = CH(C ₆ H _{11-c}) ₂	 I + II	<table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(83)</td> <td>88:12</td> <td>97</td> <td>—</td> </tr> <tr> <td>(82)</td> <td>96:4</td> <td>36</td> <td>20</td> </tr> </tbody> </table>	I+II	I:II	I	II	(83)	88:12	97	—	(82)	96:4	36	20	501						
			I+II	I:II	I	II																
(83)	88:12	97	—																			
(82)	96:4	36	20																			
<i>l</i>	34b , CH ₂ Cl ₂ , 0°, 12 h	(83)	88:12	97	—	501																
<i>l</i>	36a , CH ₂ Cl ₂ , 0°, 14 h	(82)	96:4	36	20	125																
C ₁₇	 BHT	 I + II	<table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(64)</td> <td>99:1</td> <td>—</td> <td>—</td> </tr> <tr> <td colspan="4">I ee = 95%</td> </tr> </tbody> </table>	I+II	I:II	I	II	(64)	99:1	—	—	I ee = 95%				488						
			I+II	I:II	I	II																
			(64)	99:1	—	—																
I ee = 95%																						
<i>l</i>	75 , CH ₂ Cl ₂ , rt	(64)	I:II = 99:1	I ee = 95%	488																	
<i>l</i>	75 , CH ₂ Cl ₂ , rt	(80)	I:II = 93:7	I ee = 90%	488																	
<i>l</i>		 I + II	<table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>ee (%)</th> <th>abs stereochem</th> </tr> </thead> <tbody> <tr> <td>(85)</td> <td>94:6</td> <td>99</td> <td>—</td> <td>1R,2R</td> <td>1R,2S</td> </tr> <tr> <td>I (79)</td> <td>96:4</td> <td>94</td> <td>—</td> <td>1S,2S</td> <td>1S,2R</td> </tr> </tbody> </table>	I+II	I:II	I	II	ee (%)	abs stereochem	(85)	94:6	99	—	1R,2R	1R,2S	I (79)	96:4	94	—	1S,2S	1S,2R	126
			I+II	I:II	I	II	ee (%)	abs stereochem														
			(85)	94:6	99	—	1R,2R	1R,2S														
I (79)	96:4	94	—	1S,2S	1S,2R																	
<i>l</i>	34b , CHCl ₃ , rt	(85)	94:6	99	—	1R,2R	1R,2S															
<i>l</i>	75 , CH ₂ Cl ₂ , rt	I (79)	96:4	94	—	1S,2S	1S,2R															

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																					
		75, CH ₂ Cl ₂ , rt		488																					
			<table border="1"> <thead> <tr> <th colspan="2"></th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(81)</td> <td>94:6</td> <td>96</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(90)</td> <td>94:6</td> <td>87</td> <td>—</td> <td>—</td> <td>—</td> </tr> </tbody> </table>			ee (%)		abs stereochem		I+II	I:II	I	II	I	II	(81)	94:6	96	—	—	—	(90)	94:6	87	—
		ee (%)		abs stereochem																					
I+II	I:II	I	II	I	II																				
(81)	94:6	96	—	—	—																				
(90)	94:6	87	—	—	—																				
	<table border="1"> <thead> <tr> <th>R¹</th> </tr> </thead> <tbody> <tr> <td>CF₃</td> </tr> <tr> <td>OMe</td> </tr> </tbody> </table>	R ¹	CF ₃	OMe																					
R ¹																									
CF ₃																									
OMe																									
		75, CH ₂ Cl ₂ , rt		488																					
			I:II = 94:6, I ee = 91%																						
C ₁₈		Ph-CH=CH ₂	39a, CH ₂ Cl ₂ , 0°, 21 h		468, 461																				
	R = (–)-8-phenyl-menthyl		(80) I:II = 80:20 I ee = 96% (1 <i>R</i> ,2 <i>R</i>), II ee = 91% (1 <i>R</i> ,2 <i>S</i>)																						

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 B. Non-C₂-Symmetric Complexes (See Chart 3 for Catalyst Structures)

C ₁		Ph-CH=CH ₂	120b, —		96																														
				I:II = —, I ee = —, II ee = —																															
C ₃		TMSO-CH=CH ₂	120b, benzene, 80°		457																														
				(53) I:II = 72:28 I ee = 30%, II ee = 30%																															
		TMSO-CH=CH ₂	Catalyst, benzene, 50°		457																														
			Catalyst	<table border="1"> <thead> <tr> <th colspan="2"></th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>120a</td> <td>(56)</td> <td>73:27</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>120b</td> <td>(62)</td> <td>78:22</td> <td>41</td> <td>0</td> <td>1<i>R</i> —</td> </tr> <tr> <td>120c</td> <td>(48)</td> <td>75:25</td> <td>46</td> <td>25</td> <td>1<i>R</i> 1<i>S</i></td> </tr> </tbody> </table>			ee (%)		abs stereochem		I+II	I:II	I	II	I	II	120a	(56)	73:27	—	—	—	120b	(62)	78:22	41	0	1 <i>R</i> —	120c	(48)	75:25	46	25	1 <i>R</i> 1 <i>S</i>	
		ee (%)		abs stereochem																															
I+II	I:II	I	II	I	II																														
120a	(56)	73:27	—	—	—																														
120b	(62)	78:22	41	0	1 <i>R</i> —																														
120c	(48)	75:25	46	25	1 <i>R</i> 1 <i>S</i>																														
			120b, benzene, 60°		457																														
				(71) I:II = 45:55 I ee = 40% (1 <i>S</i>), II ee = 15% (1 <i>S</i>)																															
			120b, benzene, 50°		457																														
				(60) I:II = 56:44 I ee = 2%, II ee = 40% (1 <i>R</i>)																															

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TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

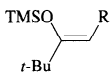
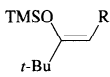
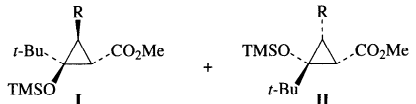
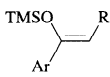
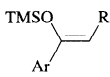
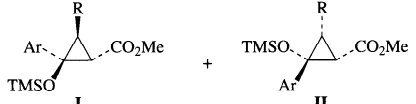
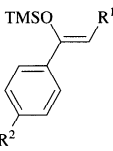
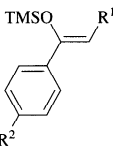
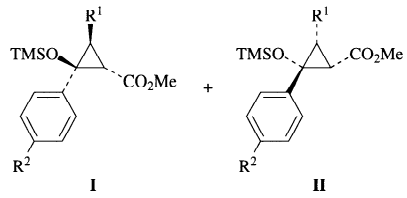
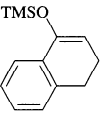
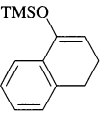
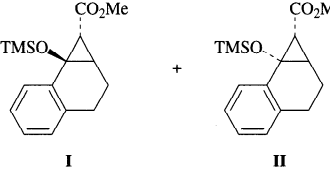
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.				
		Catalyst, DCE, 50°, 2 h		502				
					<u>R</u>	<u>Catalyst</u>	<u>ee (%)</u> <u>abs stereochem</u>	
					H	120b	<u>I+II</u> <u>I:II</u> <u>I</u> <u>II</u> <u>I</u> <u>II</u>	
					H	95a	(64) 47:53 60 76 — —	
Me	120b	(68) 41:59 61 68 — —						
Me	95a	(42) 38:62 30 8 — —						
Me	95a	(26) 38:62 32 6 — —						
		Catalyst, DCE, 50°, 2 h						
					<u>R</u> <u>Ar</u>	<u>Catalyst</u>	<u>ee (%)</u> <u>abs stereochem</u>	
					H Ph	120b	<u>I+II</u> <u>I:II</u> <u>I</u> <u>II</u> <u>I</u> <u>II</u>	
					H Ph	95a	(59) 47:53 33 38 — —	
					H Ph	95b	(46) 44:56 44 63 — —	
					H Ph	95b	(60) 47:53 21 35 — —	
					Me Ph	120b	(35) 52:48 68 71 — —	
					Me Ph	95a	(39) 47:53 75 82 — —	
Me Ph	95b	(40) 62:38 53 33 — —						
Me 4-FC ₆ H ₄	120b	(58) 61:39 47 54 — —						
Me 4-FC ₆ H ₄	95a	(44) 59:41 61 69 — —						
		95a, DCE, 50°, 5 h		460				
					<u>R¹</u> <u>R²</u>		<u>ee (%)</u> <u>abs stereochem</u>	
					H OMe		<u>I+II</u> <u>I:II</u> <u>I</u> <u>II</u> <u>I</u> <u>II</u>	
					H Me		(63) 36:64 65 73 — —	
					H CF ₃		(67) 42:58 59 74 — —	
					H NO ₂		(61) 48:52 33 60 — —	
					Me OMe		(41) 46:54 41 60 — —	
					Me Me		(40) 59:41 53 60 — —	
					Me Me		(49) 56:44 69 78 — —	
Me CF ₃		(32) 57:43 74 78 — —						
Me NO ₂		(49) 61:39 64 74 — —						
		Catalyst, DCE, 50°, 2 h		502				
					<u>Catalyst</u>		<u>ee (%)</u> <u>abs stereochem</u>	
					120b		<u>I+II</u> <u>I:II</u> <u>I</u> <u>II</u> <u>I</u> <u>II</u>	
95a		(55) 35:65 54 67 — —						
95b		(51) 31:69 65 80 — —						
95b		(39) 32:68 44 53 — —						

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst, DCE, 50°, 2 h	 I + II	502
		Catalyst	ee (%) abs stereochem	
		120b	(47) 38:62 47 34 — —	
		95a	(37) 33:67 49 46 — —	
C₄		91e , neat, rt, 5 h	 I + II	116
			ee (%) abs stereochem	
	R	120b	(47) 21:79 — — — —	
	CH ₂ Br	(73)	16:84 51 90 — 1 <i>R</i>	
	CH ₂ Cl	(71)	12:88 31 85 — 1 <i>R</i>	
	CHCl ₂	(59)	15:85 11 91 — 1 <i>R</i>	
	CCl ₃			
		90 , 60°	 I + II	114
		<i>ent</i> - 90 , 60°	(72) 70:30 6 — 1 <i>R,2R</i> —	114
		91e , CH ₃ CN, PhNHNH ₂ , 50°	(—) — 6 — 1 <i>S,2S</i> —	494
		91l , CH ₃ CN, PhNHNH ₂ , 50°	(30) 74:26 83 88 — —	494
		91m , CH ₃ CN, PhNHNH ₂ , 50°	(33) 74:26 74 53 — —	494
		91n , CH ₃ CN, PhNHNH ₂ , 50°	(37) 71:29 86 82 — —	494
		91n , CH ₃ CN, PhNHNH ₂ , 50°	(42) 75:25 77 87 — —	494
		99 , neat, 60°, 6 h	(72) 70:30 6 6 — —	113
		120d , CH ₃ CN, PhNHNH ₂ , 50°	(50) 85:15 67 63 — —	494
		120d , CH ₂ Cl ₂ , PhNHNH ₂ , 50°	(35) 84:16 41 37 — —	494
		120d , DCE, PhNHNH ₂ , 50°	(39) 79:21 29 32 — —	494
		120d , toluene, PhNHNH ₂ , 50°	(35) 79:21 8 5 — —	494
		126a , neat, 50°, 1 h	(45) 70:30 18 0 1 <i>S,2S</i> —	484
		126b , neat, 50°, 1 h	(50) 72:28 4 0 1 <i>S,2S</i> —	484
		127a , neat, 60°, 2 h	(46) 70:30 57 75 1 <i>R,2R</i> 1 <i>R,2S</i>	485
		127b , neat, 60°, 2 h	(40) 65:35 57 75 1 <i>R,2R</i> 1 <i>R,2S</i>	485
		128a , neat, 60°, 2 h	(52) 72:28 64 74 1 <i>R,2R</i> 1 <i>R,2S</i>	485
		128b , neat, 60°, 2 h	(59) 71:29 66 70 1 <i>R,2R</i> 1 <i>R,2S</i>	485
		129 , neat, 60°, 2 h	(58) 69:31 59 66 1 <i>R,2R</i> 1 <i>R,2S</i>	485
		131 , —	(—) — <2 — —	481
		132 , —	(—) — <2 — —	481
		133a , —	(—) — 3-4 — —	481
		133b , —	(—) — 3-4 — —	481
		134a , —	(—) — 10-11 — —	481
		134b , —	(—) — 0 — —	481
		134c , —	(—) — 0 — —	481
		134d , —	(—) — 0 — —	481
		135a , —	(—) — 10-11 — —	481
		135b , —	(—) — 0 — —	481
		135c , —	(—) — 0 — —	481
		135d , —	(—) — 0 — —	481
		136 , CH ₂ Cl ₂ , rt, 2 h	(62) 64:36 2 2 1 <i>S,2S</i> 1 <i>R,2S</i>	474
		137 , CH ₂ Cl ₂ , rt, 2 h	(54) 58:42 20 8 1 <i>R,2R</i> 1 <i>S,2R</i>	474
		138 , CH ₂ Cl ₂ , rt, 24 h	(6) 59:41 1 21 1 <i>R,2R</i> 1 <i>R,2S</i>	474
		139 , CH ₂ Cl ₂ , rt, 10 h	(13) 69:31 8 15 1 <i>R,2R</i> 1 <i>S,2R</i>	474
		140 , CH ₂ Cl ₂ , rt, 2 h	(61) 70:30 9 9 1 <i>R,2R</i> 1 <i>R,2S</i>	474
		141a , CH ₂ Cl ₂ , 50°, 2 h	(54) 76:24 5 10 1 <i>S,2S</i> 1 <i>S,2R</i>	503
		141b , CH ₂ Cl ₂ , 50°, 2 h	(53) 72:28 2 12 1 <i>R,2R</i> 1 <i>R,2S</i>	503
		141c , CH ₂ Cl ₂ , 50°, 2 h	(54) 79:21 6 18 1 <i>R,2R</i> 1 <i>R,2S</i>	503

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.	
	141d, CH ₂ Cl ₂ , 50°, 2 h	(45)	73:27	5	3	1 <i>S</i> ,2 <i>S</i>	1 <i>R</i> ,2 <i>S</i>	503
	141e, CH ₂ Cl ₂ , 50°, 2 h	(55)	72:28	6	1	1 <i>S</i> ,2 <i>S</i>	1 <i>R</i> ,2 <i>S</i>	503
	141f, CH ₂ Cl ₂ , 50°, 2 h	(46)	80:20	58	46	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	503
	141g, CH ₂ Cl ₂ , 50°, 2 h	(37)	78:22	53	35	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	503
	141h, CH ₂ Cl ₂ , 50°, 2 h	(65)	64:36	13	10	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	503
	142a, CH ₂ Cl ₂ , 50°, 2 h	(45)	74:26	40	10	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	503
	142b, CH ₂ Cl ₂ , 50°, 2 h	(48)	79:21	52	32	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	503
	143a, DCE, PhNHNH ₂ , rt	(92)	67:33	48	84	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	504
	144, —	(—)	—	1-8	1-8	—	—	505
	145, —	(—)	—	1-8	1-8	—	—	505
	146, —	(—)	—	1-8	1-8	—	—	505
	147a, DCE, reflux, 8 h	(23)	69:31	10	3	—	—	506
	147b, CHCl ₃ , reflux, 8 h	(71)	69:31	38	23	—	—	506
	147b, DCE, reflux, 8 h	(65)	69:31	28	22	—	—	506
	147b, benzene, reflux, 8 h	(69)	72:28	35	25	—	—	506
	147c, CHCl ₃ , reflux, 8 h	(63)	68:32	34	22	—	—	506
	147c, benzene, reflux, 8 h	(75)	69:31	32	28	—	—	506
	147d, CHCl ₃ , reflux, 8 h	(77)	65:35	45	26	—	—	506
	147e, CHCl ₃ , reflux, 8 h	(91)	72:28	27	22	—	—	506
	148a, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	ent-148a, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148b, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	ent-148b, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148c, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148d, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148e, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148f, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148g, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148h, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148i, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148j, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148k, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	148l, rt, 2 h	(—)	62:38	4-7	4-7	—	—	507
	149a, DCE, rt, 24 h	(70)	61:39	10	8	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	508
	149b, DCE, rt, 24 h	(50)	59:41	13	21	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	508
	149c, DCE, rt, 24 h	(59)	61:39	5	10	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	508
	149d, DCE, rt, 24 h	(53)	60:40	5	11	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	508
	149e, DCE, rt, 24 h	(53)	58:42	10	9	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	508
	149f, DCE, rt, 24 h	(32)	59:41	10	9	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	508
	149g, DCE, rt, 24 h	(64)	58:42	7	9	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	508
	152a, DCE, rt, 24 h	(63)	65:35	18	19	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	465
	152b, DCE, rt, 24 h	(37)	63:37	1	0	1 <i>R</i> ,2 <i>R</i>	—	465
	152c, DCE, rt, 24 h	(84)	62:38	38	5	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	465
	152d, DCE, rt, 24 h	(76)	62:38	4	0	1 <i>R</i> ,2 <i>R</i>	—	465
	153a, DCE, rt, 24 h	(76)	62:38	4	1	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	465
	153b, DCE, rt, 24 h	(74)	63:37	4	7	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	465
	154a, 55°, 2 h	(53)	24:76	40	62	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	509
	154b, CH ₂ Cl ₂ , 12 h	(46)	40:60	81	85	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	493
	155a, DCE, rt, 24 h	(52)	44:56	31	51	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	510
	155a, DCE, 0°, 24 h	(64)	37:63	37	57	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	510
	155a, DCE, -78°, 24 h	(48)	37:63	40	60	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	510
	155b, CH ₂ Cl ₂ , 12 h	(49)	69:31	25	18	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	493
	155c, CH ₂ Cl ₂ , 12 h	(49)	62:38	9	4	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	493
	156a, neat, rt, 3 h	(89)	65:35	23	16	—	—	511
	156a/MeCN, neat, rt, 2.5 h	(81)	60:40	<5	<10	—	—	511
	156a/MeCN, MeCN, 50°, 7 h	(73)	80:20	—	—	—	—	511

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)


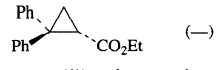
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.	
		Zeolite-156b, CH ₂ Cl ₂ , rt, 6 h	(100)	53:47	<5	<5	—	512a
		Zeolite-156b/MeCN, neat, rt, 96 h	(85)	66:34	<5	<5	—	512a
		Zeolite-156b/MeCN, MeCN, 50°, 47 h	(81)	78:22	12	7	—	512a
		157a, neat, rt, 4 h	(80)	62:38	<1	<1	—	511
		157b, neat, rt, 3 h	(82)	67:33	<5	<5	—	511
		Zeolite-157c, neat, rt, 5 h	(32)	48:52	11	5	—	512a
		Zeolite-157d, neat, rt, 51 h	(48)	43:57	<5	<5	—	512a
		158a, neat, rt, 1 h	(91)	65:35	0	0	—	511
		Zeolite-158b, neat, rt, 20 h	(66)	55:45	<5	<5	—	512a
		Catalyst, neat, heat, 2 h						
					(-)			
				<u>ee (%)</u>	<u>abs stereochem</u>			
		99	55°	11	1S			513
		100	55°	1	1R			513
		101	55°	9	1S			513
		102	50°	4	1S			513
		103	60°	1	1R			513
		104	55°	1	1S			513
		105a	80°	—	—			513
		105b	55°	0	—			513
		106	55°	1	1R			513
		107	55°	3	1S			513
		108	55°	2	1S			513
		109	55°	10	1S			513
		110a	55°	9	1R			513
		110b	55°	1	1R			513
		111	55°	1	1R			513
		112	55°	7	1R			513
		113a	55°	4	1S			513
		113b	55°	6	1R			513
		114	60°	0	—			513
		115a	55°	2	1R			513
		115b	55°	13	1R			513
		116	55°	3	1S			513
		117a	55°	4	1S			513
		117b	55°	3	1S			513
		118a	65°	13	1S			513
		118b	55°	4	1S			513
		119a	60°	52	1S			513
		119b	55°	45	1S			513
		119c	55°	66	1S			513
		119d	50°	38	1S			513
		121	60°	1	1S			513
		122	55°	6	1R			513
		123	80°	5	1S			513
		124	55°	16	1S			513
		125	55°	2	1S			513
		148a	rt	3-14	—			507 ^a
		<i>ent</i> -148a	rt	3-14	—			507 ^a
		148b	rt	3-14	—			507 ^a
		<i>ent</i> -148b	rt	3-14	—			507 ^a
		148c	rt	3-14	—			507 ^a
		148d	rt	3-14	—			507 ^a
		148e	rt	3-14	—			507 ^a
		148f	rt	3-14	—			507 ^a
		148g	rt	3-14	—			507 ^a
		148h	rt	3-14	—			507 ^a
		148i	rt	3-14	—			507 ^a
		148j	rt	3-14	—			507 ^a
		148k	rt	14	—			507 ^a

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																														
				512b																																														
		<i>ent</i> - 91c , cyclohexane, 40°																																																
		<i>ent</i> - 91c , neat, 40°																																																
		91e , cyclohexane, 40°																																																
		91e , neat, 40°																																																
		98 , cyclohexane, 40°																																																
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I+II	I:II	ee (%)				abs stereochem																																												
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(88)	64:36	3	14	—	—																																													
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(68)	62:38	<2	<2	—	—																																													
(72)	64:36	12	11	—	—																																													
		120b , —		96																																														
C₆																																																		
		143a , DCE, PhNHNH ₂ , rt																																																
		147b , CHCl ₃ , reflux, 8 h																																																
		147d , CHCl ₃ , reflux, 8 h																																																
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I+II	I:II	ee (%)				abs stereochem																																												
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(56)	86:14	47	87	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																													
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C₈				141																																														
		Catalyst, benzene, reflux																																																
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		92a	24 h	(36) 92																																														
		92b	32 h	(21) 73																																														
		92c	24 h	(48) 100																																														
		93	10 h	(43) 98																																														
C₁₂				116																																														
		91e , neat, rt, 5 h																																																
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I+II	I:II	ee (%)				abs stereochem																																												
		I	II	I	II																																													
(56)	17:83	23	95	—	1 <i>R</i>																																													
(59)	17:83	23	—	—	—																																													
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		Menthyl stereochemistry																																																
		<i>l</i>		(—)	82:18 81 78 1 <i>R</i> ,2 <i>R</i> — 116																																													
		<i>l</i>		(—)	86:14 69 54 1 <i>S</i> ,2 <i>S</i> — 116																																													
		<i>l</i>	115c , cyclohexane, reflux, 8 h	(76)	98:2 95 — 1 <i>R</i> ,2 <i>R</i> — 514																																													
		<i>l</i>	<i>ent</i> - 115c , cyclohexane, reflux, 8 h	(72)	95:5 98 — 1 <i>S</i> ,2 <i>S</i> — 514																																													
		<i>d</i>	128a , neat, 50°, 3 h	(50)	86:14 40 4 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 485																																													
		<i>l</i>	128a , neat, 50°, 3 h	(60)	83:17 65 72 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i> 485																																													
		<i>d</i>	128b , neat, 50°, 3 h	(71)	85:15 35 8 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 485																																													
		<i>l</i>	128b , neat, 50°, 3 h	(73)	83:17 75 75 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i> 485																																													
		<i>d</i>	143a , DCE, PhNHNH ₂ , rt	(66)	83:17 63 84 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 504																																													
		<i>l</i>	143a , DCE, PhNHNH ₂ , rt	(34)	82:18 66 86 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 504																																													
		<i>d</i>	143b , DCE, PhNHNH ₂ , rt	(62)	82:18 56 82 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 504																																													
		<i>d</i>	143c , DCE, PhNHNH ₂ , rt	(66)	82:18 62 82 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 504																																													
		<i>d</i>	143d , DCE, PhNHNH ₂ , rt	(28)	83:17 53 74 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 504																																													
		<i>d</i>	143e , DCE, PhNHNH ₂ , rt	(45)	83:17 39 56 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 504																																													
		<i>d</i>	143f , DCE, PhNHNH ₂ , rt	(60)	82:18 65 83 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 504																																													
		<i>d</i>	<i>ent</i> - 143g , DCE, PhNHNH ₂ , rt	(48)	86:14 57 55 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i> 504																																													
		<i>l</i>	147b , CHCl ₃ , reflux, 8 h	(81)	77:23 52 55 — — 506																																													
		<i>l</i>	147d , CHCl ₃ , reflux, 8 h	(63)	75:25 54 64 — — 506																																													

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)


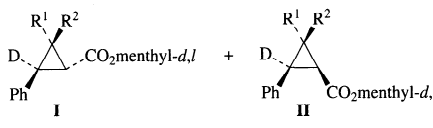
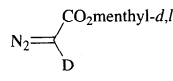

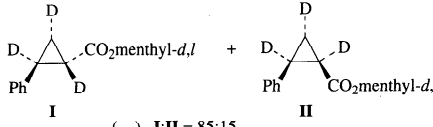
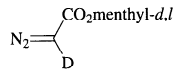
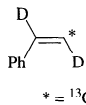
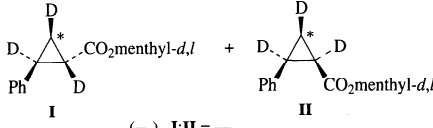
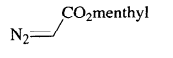
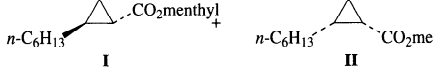
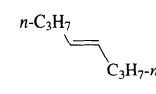
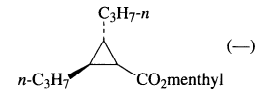
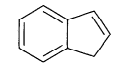
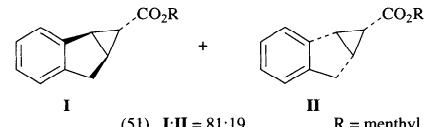

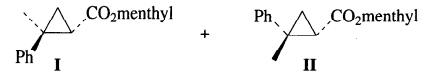
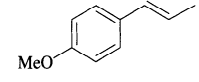
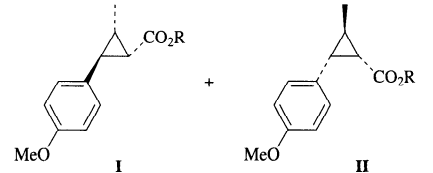
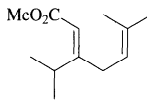
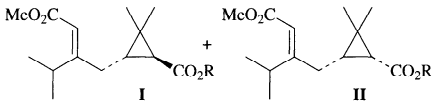

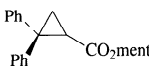
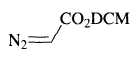
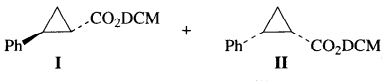
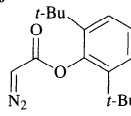
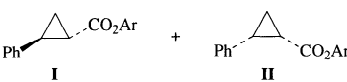
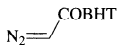
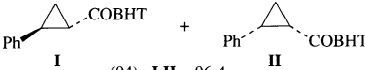
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
<i>d,l</i> -menthyl		<i>ent</i> - 91d , —	 <table border="1"> <thead> <tr> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(50-60)</td> <td>85:15</td> <td>70-80</td> <td>—</td> </tr> <tr> <td>(50-60)</td> <td>85:15</td> <td>70-80</td> <td>—</td> </tr> </tbody> </table>	ee (%)		abs stereochem		I+II	I:II	I	II	(50-60)	85:15	70-80	—	(50-60)	85:15	70-80	—	515				
ee (%)		abs stereochem																						
I+II	I:II	I	II																					
(50-60)	85:15	70-80	—																					
(50-60)	85:15	70-80	—																					
	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>D</td> <td>H</td> </tr> <tr> <td>H</td> <td>D</td> </tr> </tbody> </table>	R ¹	R ²	D	H	H	D																	
R ¹	R ²																							
D	H																							
H	D																							
		<i>ent</i> - 91d , —	 (—) I:II = 85:15 I ee = 90% (1 <i>S</i> ,2 <i>S</i> ,3 <i>S</i>), II ee = 90%	516																				
	 * = ¹³ C	<i>ent</i> - 91d , —	 (—) I:II = — I ee = 90% (1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i>), II ee = —	517																				
	<i>n</i> -C ₆ H ₁₃																							
Menthyl stereochemistry			<table border="1"> <thead> <tr> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(—)</td> <td>78:22</td> <td>84</td> <td>64</td> </tr> <tr> <td>(—)</td> <td>83:17</td> <td>76</td> <td>46</td> </tr> </tbody> </table>	ee (%)		abs stereochem		I+II	I:II	I	II	(—)	78:22	84	64	(—)	83:17	76	46					
ee (%)		abs stereochem																						
I+II	I:II	I	II																					
(—)	78:22	84	64																					
(—)	83:17	76	46																					
<i>l</i>		91e , —		116																				
<i>l</i>		<i>ent</i> - 91e , —		116																				
<i>l</i> -menthyl		91e , — <i>ent</i> - 91e , —	 (—) <table border="1"> <thead> <tr> <th colspan="2">ee (%)</th> <th>abs stereochem</th> </tr> <tr> <th>I</th> <th>II</th> <th></th> </tr> </thead> <tbody> <tr> <td>84</td> <td>—</td> <td>2<i>R</i>,3<i>R</i></td> </tr> <tr> <td>82</td> <td>—</td> <td>2<i>S</i>,3<i>S</i></td> </tr> </tbody> </table>	ee (%)		abs stereochem	I	II		84	—	2 <i>R</i> ,3 <i>R</i>	82	—	2 <i>S</i> ,3 <i>S</i>	116								
ee (%)		abs stereochem																						
I	II																							
84	—	2 <i>R</i> ,3 <i>R</i>																						
82	—	2 <i>S</i> ,3 <i>S</i>																						
<i>d</i> -menthyl		143a , DCE, PhNHNH ₂ , rt	 (51) I:II = 81:19 I ee = 52%, II ee = 81% R = menthyl	504																				
																								
Menthyl stereochemistry			<table border="1"> <thead> <tr> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(—)</td> <td>64:36</td> <td>58</td> <td>68</td> </tr> <tr> <td>(—)</td> <td>60:40</td> <td>68</td> <td>86</td> </tr> <tr> <td>(30)</td> <td>63:37</td> <td>72</td> <td>82</td> </tr> </tbody> </table>	ee (%)		abs stereochem		I+II	I:II	I	II	(—)	64:36	58	68	(—)	60:40	68	86	(30)	63:37	72	82	
ee (%)		abs stereochem																						
I+II	I:II	I	II																					
(—)	64:36	58	68																					
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<i>l</i>		91e , —		116																				
<i>l</i>		<i>ent</i> - 91e , —		116																				
<i>d</i>		143a , DCE, PhNHNH ₂ , rt		504																				
<i>d</i> -menthyl		143a , DCF, PhNHNH ₂ , rt	 (29) I:II = 81:19 I ee = 64%, II ee = 74% R = menthyl	504																				

TABLE V. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL COPPER CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<i>l</i> -menthyl		91e , cyclohexane, 35°	 (70) I:II = 44:66 I ee = >95%, II ee = >95% R = <i>l</i> -menthyl	512b												
<i>d</i> -menthyl		143a , DCE, PhNHNH ₂ , rt	 (27) 59% ee	504												
C ₁₅		Catalyst, CHCl ₃ , reflux, 8 h	 ee (%) <table border="1" data-bbox="1093 700 1336 792"> <thead> <tr> <th colspan="2">Catalyst</th> <th colspan="2">I:II</th> </tr> </thead> <tbody> <tr> <td>147b</td> <td>(64)</td> <td>86:14</td> <td>45 47</td> </tr> <tr> <td>147d</td> <td>(54)</td> <td>86:14</td> <td>64 63</td> </tr> </tbody> </table>	Catalyst		I:II		147b	(64)	86:14	45 47	147d	(54)	86:14	64 63	506
Catalyst		I:II														
147b	(64)	86:14	45 47													
147d	(54)	86:14	64 63													
C ₁₆		143a , DCE, PhNHNH ₂ , rt	 (73) I:II = 93:7 Ar = 2,6-(<i>t</i> -Bu) ₂ C ₆ H ₃ I ee = 9%, II ee = —	504												
C ₁₇		155a , DCE, rt, 24 h	 (94) I:II = 96:4 I ee = 10%, II ee = —	510												

^a The authors do not indicate whether or not the reaction was run neat.

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS

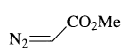

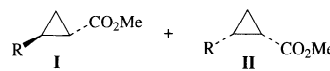
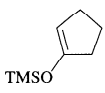
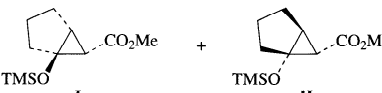

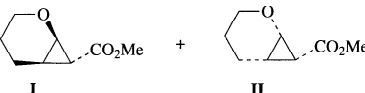
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
<i>(See Chart 4 for Catalyst Structures)</i>												
C_3 		Catalyst, CH ₂ Cl ₂ , reflux		309								
					Catalyst		ee (%) abs stereochem					
					<i>n</i> -Pr	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	I:II (55)	I:II (58:42)	I (44)	II (40)	—	—
					<i>n</i> -Pr	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(21)	38:62	42	56	—	—
					CH ₂ OAc	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(46)	55:45	56	44	—	—
					CH ₂ OAc	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(11)	47:53	4	10	—	—
					OAc	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(62)	53:47	10	55	—	—
					OAc	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(14)	44:56	56	68	—	—
					O ₂ CPh	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(40)	50:50	22	54	—	—
					O ₂ CPh	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(22)	38:62	32	54	—	—
	Catalyst, CH ₂ Cl ₂ , reflux	Catalyst		309								
					Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(36) I:II = 43:53; I ee = 50%, II ee = 14%						
					Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(5) I:II = 57:43; I ee = —%, II ee = —%						
	Catalyst, CH ₂ Cl ₂ , reflux	Catalyst		309								
					Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(18) I:II = 87:13; I ee = 10%, II ee = 49%						
					Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(31) I:II = 71:29; I ee = 14%, II ee = 76%						

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)



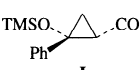
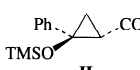
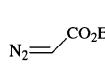

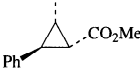
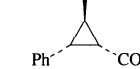
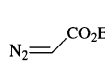

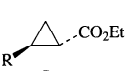
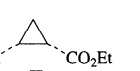

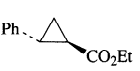
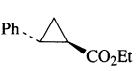
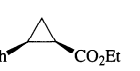
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		Catalyst Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a) Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(80) I:II = 45:55; I ee = 30%, II ee = 14% (44) I:II = 47:53; I ee = 14%, II ee = 10%																																																																																																																																																																																										
		Catalyst, CH ₂ Cl ₂ , reflux	 + 	309																																																																																																																																																																																									
		Catalyst Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a) Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(12) I:II = 99:1; I ee = —%, II ee = —% (10) I:II = 89:11; I ee = —%, II ee = —%																																																																																																																																																																																										
C ₄ 		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux	 + 																																																																																																																																																																																										
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<table border="1"> <thead> <tr> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(80)</td> <td>55:45</td> <td>6</td> <td>30</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> </tr> <tr> <td>(98)</td> <td>31:69</td> <td>57</td> <td>53</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(76)</td> <td>57:43</td> <td>12</td> <td>6</td> <td>—</td> <td>—</td> </tr> <tr> <td>(72)</td> <td>56:44</td> <td>10</td> <td>5</td> <td>—</td> <td>—</td> </tr> <tr> <td>(65)</td> <td>52:48</td> <td>9</td> <td>4</td> <td>—</td> <td>—</td> </tr> <tr> <td>(71)</td> <td>52:48</td> <td>7</td> <td>4</td> <td>—</td> <td>—</td> </tr> <tr> <td>(71)</td> <td>51:49</td> <td>9</td> <td>6</td> <td>—</td> <td>—</td> </tr> <tr> <td>(71)</td> <td>51:49</td> <td>8</td> <td>4</td> <td>—</td> <td>—</td> </tr> <tr> <td>(69)</td> <td>52:48</td> <td>6</td> <td>3</td> <td>—</td> <td>—</td> </tr> <tr> <td>(70)</td> <td>54:46</td> <td>3</td> <td>4</td> <td>—</td> <td>—</td> </tr> <tr> <td>(69)</td> <td>52:48</td> <td>5</td> <td>2</td> <td>—</td> <td>—</td> </tr> <tr> <td>(48)</td> <td>—</td> <td>7</td> <td>3</td> <td>—</td> <td>—</td> </tr> <tr> <td>(28)</td> <td>54:46</td> <td>10</td> <td>6</td> <td>—</td> <td>—</td> </tr> <tr> <td>(33)</td> <td>55:45</td> <td>8</td> <td>7</td> <td>—</td> <td>—</td> </tr> <tr> <td>(36)</td> <td>47:53</td> <td>5</td> <td>4</td> <td>—</td> <td>—</td> </tr> <tr> <td>(12)</td> <td>58:42</td> <td>4</td> <td>3</td> <td>—</td> <td>—</td> </tr> <tr> <td>(8)</td> <td>63:37</td> <td>5</td> <td>3</td> <td>—</td> <td>—</td> </tr> <tr> <td>(78)</td> <td>55:45</td> <td>2</td> <td>2</td> <td>—</td> <td>—</td> </tr> <tr> <td>(59)</td> <td>56:44</td> <td>58</td> <td>33</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(47)</td> <td>66:34</td> <td>22</td> <td>38</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(41)</td> <td>34:66</td> <td>24</td> <td>57</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> </tr> <tr> <td>(50)</td> <td>62:38</td> <td>17</td> <td>28</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(63)</td> <td>57:43</td> <td>51</td> <td>49</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(74)</td> <td>41:59</td> <td>23</td> <td>29</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(62)</td> <td>36:64</td> <td>47</td> <td>73</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(62)</td> <td>38:62</td> <td>47</td> <td>68</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(44)</td> <td>48:52</td> <td>85</td> <td>82</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(—)</td> <td>30:70</td> <td>10</td> <td>—</td> <td>—</td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(—)</td> <td>29:71</td> <td>—</td> <td>15</td> <td>—</td> <td>1<i>R</i>,2<i>S</i></td> </tr> <tr> <td>(—)</td> <td>60:40</td> <td>14</td> <td>5</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> </tbody> </table>	ee (%)		abs stereochem		I+II	I:II	I	II	(80)	55:45	6	30	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	(98)	31:69	57	53	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(76)	57:43	12	6	—	—	(72)	56:44	10	5	—	—	(65)	52:48	9	4	—	—	(71)	52:48	7	4	—	—	(71)	51:49	9	6	—	—	(71)	51:49	8	4	—	—	(69)	52:48	6	3	—	—	(70)	54:46	3	4	—	—	(69)	52:48	5	2	—	—	(48)	—	7	3	—	—	(28)	54:46	10	6	—	—	(33)	55:45	8	7	—	—	(36)	47:53	5	4	—	—	(12)	58:42	4	3	—	—	(8)	63:37	5	3	—	—	(78)	55:45	2	2	—	—	(59)	56:44	58	33	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(47)	66:34	22	38	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(41)	34:66	24	57	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	(50)	62:38	17	28	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(63)	57:43	51	49	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(74)	41:59	23	29	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(62)	36:64	47	73	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(62)	38:62	47	68	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(44)	48:52	85	82	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(—)	30:70	10	—	—	1 <i>S</i> ,2 <i>R</i>	(—)	29:71	—	15	—	1 <i>R</i> ,2 <i>S</i>	(—)	60:40	14	5	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	
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(62)	38:62	47	68	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>																																																																																																																																																																																								
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Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane Rh ₂ (<i>S</i> -BDME) ₄ (166), CH ₂ Cl ₂ , rt, 15 h 168a , neat, 30°, 3 h 168a , neat, 50°, 3 h 168a , neat, 70°, 3 h 168b , neat, 30°, 3 h 168c , neat, 30°, 3 h 168d , neat, 30°, 3 h 168e , neat, 30°, 3 h 168f , neat, 30°, 3 h 168g , neat, 30°, 3 h 168h , neat, 30°, 3 h 168i , H ₂ O, 30°, 3 h 168j , H ₂ O, 30°, 3 h 168k , H ₂ O, 30°, 3 h 168l , H ₂ O, 30°, 3 h 168m , acetone, 30°, 3 h 168n , CH ₂ Cl ₂ , 0°, 1 h Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux Rh ₂ (5 <i>S</i> -DMAP) ₄ (171c), CH ₂ Cl ₂ , reflux Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux, 13 h Rh ₂ (<i>S</i> -PTPI) ₄ (175), CH ₂ Cl ₂ , reflux, 3 h Rh ₂ (<i>S</i> -PTPI) ₄ (175), Et ₂ O, 40°, 3 h Rh ₂ (4 <i>S</i> -BNAZ) ₄ (176a), CH ₂ Cl ₂ , rt Rh ₂ (4 <i>S</i> -IBAZ) ₄ (176b), CH ₂ Cl ₂ , rt Rh ₂ (4 <i>S</i> -IBAZ) ₄ (176b), CH ₂ Cl ₂ , reflux 177 , AgOTf, THF, rt, 6 h 178a , CH ₂ Cl ₂ , 0°, 24 h 178b , CH ₂ Cl ₂ , rt 189b (Chart 5), CH ₂ Cl ₂ , rt, 24 h	518 309 309																																																																																																																																																																																												

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	 (44) I:II = 55:45; I ee = 15%, II ee = 5%	309												
		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	 ee (%) abs stereochem <table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(44)</td> <td>44:56</td> <td>12</td> <td>16</td> <td>—</td> <td>—</td> </tr> </tbody> </table>	I+II	I:II	I	II	I	II	(44)	44:56	12	16	—	—	309
I+II	I:II	I	II	I	II											
(44)	44:56	12	16	—	—											
		Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux	(19) 36:64 24 18 — — 309	309												
		178a , CH ₂ Cl ₂ , 0°, 24 h	(—) 11:89 50 20 — — 524, 100	524, 100												
		178b , CH ₂ Cl ₂ , rt	(—) 16:84 20 25 — — 518	518												
		178b , CH ₂ Cl ₂ , 0°	(—) 7:93 20 0 — — 518	518												
			 ee (%) abs stereochem <table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(—)</td> <td>19:81</td> <td>60</td> <td>45</td> <td>—</td> <td>—</td> </tr> </tbody> </table>	I+II	I:II	I	II	I	II	(—)	19:81	60	45	—	—	524, 100
I+II	I:II	I	II	I	II											
(—)	19:81	60	45	—	—											
		178b , CH ₂ Cl ₂ , rt	(—) 50:50 10 10 — — 518	518												
		178b , CH ₂ Cl ₂ , 0°	(—) 20:80 40 20 — — 518	518												
		Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux	 (32) I:II = 42:58	309												
		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	 (37) ee = 20%	309												
		Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux	 (31) I:II = 36:64	309												
		Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane	 (45) I:II = 80:20; I ee = 12%, II ee = 58%	73												
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane	 (57) I:II = 75:25; I ee = 5%, II ee = 8%	73												
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane	 (63) ee = 7%	73												
			 ee (%) abs stereochem <table border="1"> <thead> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(80)</td> <td>31:69</td> <td>57</td> <td>62</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> </tbody> </table>	I+II	I:II	I	II	I	II	(80)	31:69	57	62	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	129
I+II	I:II	I	II	I	II											
(80)	31:69	57	62	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>											
		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	(49) 52:48 56 77 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 108, 309	108, 309												
		Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux	(35) 32:68 — 57 — — 309	309												
		Rh ₂ (<i>S</i> -PTPI) ₄ (175), CH ₂ Cl ₂ , reflux, 3 h	(71) 52:48 61 51 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 519	519												
		Rh ₂ (<i>S</i> -PTPI) ₄ (175), Et ₂ O, 40°, 3 h	(65) 51:49 68 66 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i> 522	522												

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst, CH ₂ Cl ₂ , reflux		309
		Catalyst Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a) Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), 13 h	(24) I:II = 63:37; I ee = 28%, II ee = 78% (10) I:II = 53:47; I ee = 76%, II ee = 56%	
		Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux		309
			(17) I:II = 98:2; I ee = 8%, II ee = —%	
		Rh ₂ (<i>S</i> -BDME) ₄ (166), CH ₂ Cl ₂ , rt, 15 h Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux		129 309
			(59) I:II = 48:52; I ee = 35%, II ee = 87% (25) I:II = 37:63	
		Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux		309
			(28) I:II = 37:63	
		Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, -78°		213
			(75) ee = 93%	
		Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, -78°		213
			(68) ee = 86%	
		Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, 78°		213
			(57) ee = 87%	
		Catalyst, CH ₂ Cl ₂ , rt, 16 h		142
		Catalyst	ee (%)	
		163a	(36) 93	
		163b	(27) 98	
		163c	(66) 96	
		163g	(47) 95	
		163l	(—) —	
		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux Rh ₂ (4 <i>S</i> -PHOX) ₄ (173), CH ₂ Cl ₂ , reflux, 13 h		309
			(23) I:II = 54:46; I ee = 32%, II ee = 35% (10) I:II = 46:54; I ee = 46%, II ee = 44%	
		Catalyst, CH ₂ Cl ₂ , reflux		109
			ee (%) abs stereochem	
		Catalyst	I+II I:II I II I II	
		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	22 75:25 62 67 — —	
		Rh ₂ (5 <i>R</i> -MEPY) ₄ (<i>ent</i> - 171a)	21 82:18 16 12 — —	

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, -78°	 (49) ee = 76%	213
		Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, -78°	 (53) ee = 88%	213
C₉ N ₂ =C(CO ₂ Me)Ph	R-CH=CH ₂	Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane	 I + II	73
	R		ee (%) abs stereochem	
	Et		I+II I:II I II I II	
	<i>n</i> -Bu		(86) 93:7 80 — — —	
	<i>i</i> -Pr		(86) 93:7 77 — — —	
	CH ₂ OAc		(63) 87:13 74 — —	
			(85) 97:3 80 — — —	
	RO-CH=CH ₂		 I + II	
	R		ee (%) abs stereochem	
	Et	Rh ₂ (<i>S</i> -DOSP) ₄ (161a) ₄ , pentane	(88) 97:3 66 — 1 <i>R</i> ,2 <i>S</i> —	73
	Et	Rh ₂ (<i>S</i> -biTISP) ₂ (169c), CH ₂ Cl ₂ , -50°	(86) >95:5 79 — 1 <i>S</i> ,2 <i>R</i> —	525
	<i>n</i> -Bu	Rh ₂ (<i>S</i> -DOSP) ₄ (161a) ₄ , pentane	(84) 97:3 64 — 1 <i>R</i> ,2 <i>S</i> —	73
	Ph-CH=CH ₂		 I + II	
			ee (%) abs stereochem	
			I+II I:II I II I II	
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane	(90) 98:2 87 — 1 <i>R</i> ,2 <i>S</i> —	73
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane	(73) 96:4 85 — 1 <i>R</i> ,2 <i>S</i> —	74
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), CH ₂ Cl ₂	(77) 97:3 61 — 1 <i>R</i> ,2 <i>S</i> —	74
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), SC-CHEF ₃ (100 bar), 30°, 1h	(—) — 40 — — —	526
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), SC-CHEF ₃ (52 bar), 30°, 1h	(—) — 77 — — —	526
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), SC-CO ₂ (110 bar), 34°, 1h	(—) — 80 — — —	526
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), SC-CO ₂ (79 bar), 34°, 1h	(—) — 83 — — —	526
		161e , CH ₂ Cl ₂	(45) 97:3 60 — 1 <i>R</i> ,2 <i>S</i> —	74
		164a , CH ₂ Cl ₂ , reflux	(71) 98:2 35 — — —	145
		164a , benzene, reflux	(98) >99:1 40 — — —	145
		164a , pentane, reflux	(96) >99:1 49 — — —	145
		164a , cyclohexane, reflux	(88) 98:2 51 — — —	145
		164b , CH ₂ Cl ₂ , reflux	(70) 99:1 36 — — —	145
		168n , pentane	(82) 96:4 16 — 1 <i>S</i> ,2 <i>R</i> —	74
		170 , CH ₂ Cl ₂ , reflux	(86) >99:1 31 — — —	145
		Rh ₂ (<i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂	(27) 97:3 49 — 1 <i>R</i> ,2 <i>S</i> —	74
		Rh ₂ (<i>4S</i> -MEOX) ₄ (172c), CH ₂ Cl ₂	(57) 96:4 41 — 1 <i>R</i> ,2 <i>S</i> —	74
		Rh ₂ (<i>4S</i> -MBOIM) ₄ (174a), CH ₂ Cl ₂	(73) 96:4 48 — 1 <i>R</i> ,2 <i>S</i> —	74
		Rh ₂ (<i>4S</i> -TBOIM) ₄ (174b), CH ₂ Cl ₂	(63) 95:5 77 — 1 <i>R</i> ,2 <i>S</i> —	74
		Rh ₂ (<i>4S</i> -TBOIM) ₄ (174b), pentane	(69) 94:6 75 — 1 <i>R</i> ,2 <i>S</i> —	74

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

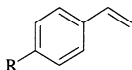
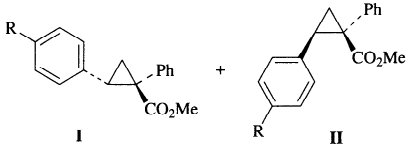



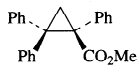
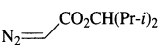
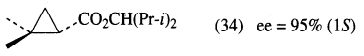

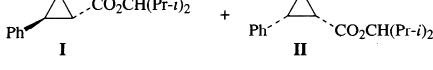
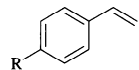
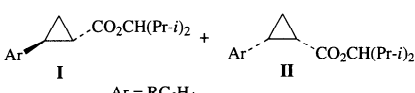
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																														
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(82)	98:2	88	—	1 <i>R</i> ,2 <i>S</i>	—																																																													
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						Rh ₂ (<i>S</i> -PTPI) ₄ (175), solvent, 40°, 3 h		<table border="1"> <thead> <tr> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(73)</td> <td>74:26</td> <td>49</td> <td>63</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(66)</td> <td>70:30</td> <td>42</td> <td>59</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(75)</td> <td>63:37</td> <td>7</td> <td>22</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(44)</td> <td>66:34</td> <td>79</td> <td>76</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(73)</td> <td>74:26</td> <td>98</td> <td>96</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(42)</td> <td>71:29</td> <td>79</td> <td>82</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(66)</td> <td>71:29</td> <td>79</td> <td>81</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> </tbody> </table>	ee (%)		abs stereochem		I+II	I:II	I	II	(73)	74:26	49	63	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(66)	70:30	42	59	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(75)	63:37	7	22	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(44)	66:34	79	76	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(73)	74:26	98	96	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(42)	71:29	79	82	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(66)	71:29	79	81	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	522, 519 522 522 522 522 522 522							
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TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																								
$n\text{-C}_6\text{H}_{13}$		$\text{Rh}_2(\text{S-PTPI})_4$ (175), Et_2O , reflux, 3 h	 (52) I:II = 71:29 I ee = 89% (1 <i>S</i> ,2 <i>S</i>), II ee = 82% (1 <i>S</i> ,2 <i>R</i>) R = CH(<i>Pr</i> - <i>i</i>) ₂	522																																																																								
		$\text{Rh}_2(\text{S-PTPI})_4$ (175), Et_2O , reflux, 3 h	 (80) I:II = 54:46 I ee = 94% (1 <i>S</i> ,2 <i>S</i>), II ee = 95% (1 <i>S</i> ,2 <i>R</i>) R = CH(<i>Pr</i> - <i>i</i>) ₂	522																																																																								
		$\text{Rh}_2(\text{S-PTPI})_4$ (175), Et_2O , reflux, 3 h	 (77) ee = 95% (1 <i>S</i>) R = CH(<i>Pr</i> - <i>i</i>) ₂	522																																																																								
C_{10}		$\text{Rh}_2(\text{S-PTPI})_4$ (175), Et_2O , reflux, 3 h	 (92) I:II = 62:38 I ee = 65% (1 <i>S</i> ,2 <i>S</i>), II ee = 52% (1 <i>S</i> ,2 <i>R</i>) R = CMe(<i>Pr</i> - <i>i</i>) ₂	519																																																																								
		$\text{Rh}_2(\text{S-PTPI})_4$ (175), Et_2O , reflux, 3 h	 (51) I:II = 73:27 I ee = 67% (1 <i>S</i> ,2 <i>S</i>), II ee = 83% (1 <i>S</i> ,2 <i>R</i>)	108																																																																								
C_{10}		Catalyst, CH_2Cl_2 , -50° to rt, 15 h	 (32) I:II = 67:33 (63) I:II = 70:30 (5) I:II = 62:38 (38) I:II = 67:33 (24) I:II = 64:36 (43) I:II = 67:33 (8) I:II = 50:50 (26) I:II = 69:31 (7) I:II = 67:33	527																																																																								
C_{11}	R = Me		<table border="1"> <thead> <tr> <th rowspan="2">Catalyst</th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>163a</td> <td>(32)</td> <td>67:33</td> <td>49</td> <td>58</td> <td>—</td> <td>—</td> </tr> <tr> <td>163b</td> <td>(63)</td> <td>70:30</td> <td>69</td> <td>71</td> <td>—</td> <td>—</td> </tr> <tr> <td>163c</td> <td>(5)</td> <td>62:38</td> <td>57</td> <td>52</td> <td>—</td> <td>—</td> </tr> <tr> <td>163d</td> <td>(38)</td> <td>67:33</td> <td>71</td> <td>80</td> <td>—</td> <td>—</td> </tr> <tr> <td>163f</td> <td>(24)</td> <td>64:36</td> <td>33</td> <td>33</td> <td>—</td> <td>—</td> </tr> <tr> <td>163h</td> <td>(43)</td> <td>67:33</td> <td>21</td> <td>21</td> <td>—</td> <td>—</td> </tr> <tr> <td>163i</td> <td>(8)</td> <td>50:50</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>163j</td> <td>(26)</td> <td>69:31</td> <td>67</td> <td>51</td> <td>—</td> <td>—</td> </tr> <tr> <td>163k</td> <td>(7)</td> <td>67:33</td> <td>33</td> <td>33</td> <td>—</td> <td>—</td> </tr> </tbody> </table>	Catalyst	ee (%)		abs stereochem		I+II	I:II	I	II	163a	(32)	67:33	49	58	—	—	163b	(63)	70:30	69	71	—	—	163c	(5)	62:38	57	52	—	—	163d	(38)	67:33	71	80	—	—	163f	(24)	64:36	33	33	—	—	163h	(43)	67:33	21	21	—	—	163i	(8)	50:50	—	—	—	—	163j	(26)	69:31	67	51	—	—	163k	(7)	67:33	33	33	—	—	
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	I+II	I:II	I	II																																																																								
163a	(32)	67:33	49	58	—	—																																																																						
163b	(63)	70:30	69	71	—	—																																																																						
163c	(5)	62:38	57	52	—	—																																																																						
163d	(38)	67:33	71	80	—	—																																																																						
163f	(24)	64:36	33	33	—	—																																																																						
163h	(43)	67:33	21	21	—	—																																																																						
163i	(8)	50:50	—	—	—	—																																																																						
163j	(26)	69:31	67	51	—	—																																																																						
163k	(7)	67:33	33	33	—	—																																																																						
R = Me		$\text{Rh}_2(\text{S-TBSP})_4$ (161b), pentane, rt	 (65) I:II = 94-89:6-11 (63) I:II = 94-89:6-11 (58) I:II = 94-89:6-11	58, 128																																																																								
	R^1		<table border="1"> <thead> <tr> <th rowspan="2">R^1</th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>(65)</td> <td>94-89:6-11</td> <td>>95</td> <td>—</td> <td>—</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>(63)</td> <td>94-89:6-11</td> <td>>90</td> <td>—</td> <td>—</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(58)</td> <td>94-89:6-11</td> <td>95</td> <td>—</td> <td>—</td> </tr> </tbody> </table>	R^1	ee (%)		abs stereochem		I+II	I:II	I	II	Et	(65)	94-89:6-11	>95	—	—	<i>n</i> -Bu	(63)	94-89:6-11	>90	—	—	<i>i</i> -Pr	(58)	94-89:6-11	95	—	—																																														
R^1	ee (%)		abs stereochem																																																																									
	I+II	I:II	I	II																																																																								
Et	(65)	94-89:6-11	>95	—	—																																																																							
<i>n</i> -Bu	(63)	94-89:6-11	>90	—	—																																																																							
<i>i</i> -Pr	(58)	94-89:6-11	95	—	—																																																																							

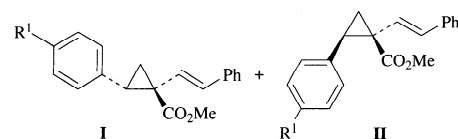
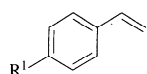
TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.													
R = Me			 														
		R ¹		<table border="1"> <thead> <tr> <th colspan="2"></th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> </table>			ee (%)		abs stereochem		I+II	I:II	I	II	I	II	
				ee (%)		abs stereochem											
		I+II	I:II	I	II	I	II										
		Ac	Rh ₂ (S-DOSP) ₄ (161a), pentane, -78°	(26) >95:5	95	—	1 <i>R</i> ,2 <i>S</i>	—	58								
		Et	Rh ₂ (S-DOSP) ₄ (161a), pentane, -78°	(65) >95:5	93	—	1 <i>R</i> ,2 <i>S</i>	—	58								
		Ac	Rh ₂ (S-TBSP) ₄ (161b), pentane, rt	(40) >95:5	76	—	1 <i>R</i> ,2 <i>S</i>	—	58, 128								
		Et	Rh ₂ (S-TBSP) ₄ (161b), pentane, rt	(83) >95:5	59	—	1 <i>R</i> ,2 <i>S</i>	—	58, 128								
		Et	163a , pentane, rt, 15 h	(78) >95:5	47	—	—	—	527								
		Et	163b , pentane, rt, 15 h	(78) >95:5	52	—	—	—	527								
		Et	163c , pentane, rt, 15 h	(76) >95:5	23	—	—	—	527								
		Et	163d , pentane, rt, 15 h	(70) >95:5	60	—	—	—	527								
		Et	163f , pentane, rt, 15 h	(69) >95:5	19	—	—	—	527								
		Et	163h , pentane, rt, 15 h	(70) >95:5	19	—	—	—	527								
		Et	163i , pentane, rt, 15 h	(70) >95:5	14	—	—	—	527								
Et	163j , pentane, rt, 15 h	(71) >95:5	47	—	—	—	527										
Et	Rh ₂ (S-bi-TISP) ₂ (169c), CH ₂ Cl ₂ , -50°	(53) >95:5	87	—	1 <i>S</i> ,2 <i>R</i>	—	525										
R = Me		Rh ₂ (S-DOSP) ₄ (161a), pentane, -78°	 (84) ee = 86%	58													
R = Me		Rh ₂ (S-DOSP) ₄ (161a), pentane	 (52) ee = 95%	58													
R = Me		Rh ₂ (S-DOSP) ₄ (161a), pentane	 (80)	58													
R = Me		Rh ₂ (S-DOSP) ₄ (161a), pentane	 (0)	58													
R = Me		Rh ₂ (S-DOSP) ₄ (161a), pentane, -78°	 (66) ee = 88%	213													
R = Me		Rh ₂ (S-DOSP) ₄ (161a), pentane, -78°	 (71) ee = 94%	213													
R = Me			 														
			<table border="1"> <thead> <tr> <th colspan="2"></th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> </table>			ee (%)		abs stereochem		I+II	I:II	I	II	I	II		
		ee (%)		abs stereochem													
I+II	I:II	I	II	I	II												
	Rh ₂ (S-DOSP) ₄ (161a), pentane	(91) 98:2	94	—	1 <i>S</i> ,2 <i>S</i>	—	73										
	Rh ₂ (S-DOSP) ₄ (161a), pentane, rt	(—) >95:5	92	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-DOSP) ₄ (161a), pentane, 35°	(—) >95:5	91	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-DOSP) ₄ (161a), pentane, -20°	(—) >95:5	93	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-DOSP) ₄ (161a), pentane, -78°	(68) >95:5	98	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-DOSP) ₄ (161a), CH ₂ Cl ₂	(—) >95:5	79	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-DOSP) ₄ (161a), hexane, 69°	(—) >95:5	86	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-DOSP) ₄ (161a), heptane, 98°	(—) >95:5	82	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-TBSP) ₄ (161b), pentane	(91) 98:2	90	—	1 <i>S</i> ,2 <i>S</i>	—	73, 128										
	Rh ₂ (S-TBSP) ₄ (161b), pentane, rt	(79) >95:5	90	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	Rh ₂ (S-TBSP) ₄ (161b), pentane, 0°, 18 h	(79) >95:5	94	—	1 <i>S</i> ,2 <i>S</i>	—	200										
	Rh ₂ (S-TBSP) ₄ (161b), CH ₂ Cl ₂ , rt	(68) >95:5	74	—	1 <i>S</i> ,2 <i>S</i>	—	58, 128										
	Rh ₂ (S-TBSP) ₄ (161b), CH ₂ Cl ₂ , -50°	(62) >95:5	92	—	1 <i>S</i> ,2 <i>S</i>	—	528										
	Rh ₂ (S-TBSP) ₄ (161b), benzene	(—) >95:5	86	—	1 <i>S</i> ,2 <i>S</i>	—	128										
	161c , CH ₂ Cl ₂	(—) >95:5	76	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	161d , CH ₂ Cl ₂	(—) >95:5	83	—	1 <i>S</i> ,2 <i>S</i>	—	58										
	161e , CH ₂ Cl ₂	(—) >95:5	74	—	1 <i>S</i> ,2 <i>S</i>	—	58, 128										

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
	161e , benzene	(—)	>95:5	87	—	—	128
	162a , CH ₂ Cl ₂	(—)	>95:5	75	—	1 <i>S</i> ,2 <i>S</i>	58
	162b , CH ₂ Cl ₂	(—)	>95:5	61	—	1 <i>S</i> ,2 <i>S</i>	58
	162c , CH ₂ Cl ₂	(—)	>95:5	30	—	1 <i>S</i> ,2 <i>S</i>	58
	163a , pentane, rt, 15 h	(75)	>95:5	64	—	1 <i>S</i> ,2 <i>S</i>	527
	163b , pentane, rt, 15 h	(91)	>95:5	76	—	1 <i>S</i> ,2 <i>S</i>	527
	163c , pentane, rt, 15 h	(68)	>95:5	59	—	1 <i>S</i> ,2 <i>S</i>	527
	163d , pentane, rt, 15 h	(84)	>95:5	48	—	1 <i>S</i> ,2 <i>S</i>	527
	163e , pentane, rt, 15 h	(43)	>95:5	36	—	1 <i>S</i> ,2 <i>S</i>	527
	163f , pentane, rt, 15 h	(52)	>95:5	40	—	1 <i>S</i> ,2 <i>S</i>	527
	163h , pentane, rt, 15 h	(74)	>95:5	7	—	1 <i>S</i> ,2 <i>S</i>	527
	163i , pentane, rt, 15 h	(13)	>95:5	20	—	1 <i>R</i> ,2 <i>R</i>	527
	163j , pentane, rt, 15 h	(55)	>95:5	64	—	1 <i>S</i> ,2 <i>S</i>	527
	163k , pentane, rt, 15 h	(71)	>95:5	55	—	1 <i>R</i> ,2 <i>R</i>	527
	164a , pentane	(—)	>95:5	81	—	1 <i>S</i> ,2 <i>S</i>	58
	165 , pentane	(—)	>95:5	81	—	1 <i>S</i> ,2 <i>S</i>	58
	167 , CH ₂ Cl ₂ , rt	(81)	>95:5	59	—	1 <i>R</i> ,2 <i>R</i>	528
	167 , CH ₂ Cl ₂ , -50°	(52)	>95:5	83	—	1 <i>R</i> ,2 <i>R</i>	528
	167 , pentane, rt	(78)	>95:5	56	—	1 <i>R</i> ,2 <i>R</i>	528
	168o , CH ₂ Cl ₂	(—)	>95:5	30	—	1 <i>S</i> ,2 <i>S</i>	58
	168p , CH ₂ Cl ₂	(—)	>95:5	6	—	1 <i>S</i> ,2 <i>S</i>	58
	Rh ₂ (<i>S</i> -biTBSP) ₂ (169a), CH ₂ Cl ₂ , rt	(52-92)	>95:5	63	—	1 <i>R</i> ,2 <i>R</i>	525
	Rh ₂ (<i>S</i> -biTBSP) ₂ (169a), hexane, rt	(52-92)	>95:5	55	—	1 <i>R</i> ,2 <i>R</i>	525
	Rh ₂ (<i>S</i> -biDOSP) ₂ (169b), CH ₂ Cl ₂ , rt	(52-92)	>95:5	68	—	1 <i>R</i> ,2 <i>R</i>	525
	Rh ₂ (<i>S</i> -biDOSP) ₂ (169b), hexane, rt	(52-92)	>95:5	53	—	1 <i>R</i> ,2 <i>R</i>	525
	Rh ₂ (<i>S</i> -biTISP) ₂ (169c), CH ₂ Cl ₂ , rt	(52-92)	>95:5	90	—	1 <i>R</i> ,2 <i>R</i>	525
	Rh ₂ (<i>S</i> -biTISP) ₂ (169c), CH ₂ Cl ₂ , -50°	(52-92)	>95:5	98	—	1 <i>R</i> ,2 <i>R</i>	525
	Rh ₂ (<i>S</i> -biTISP) ₂ (169c), hexane, rt	(52-92)	>95:5	74	—	1 <i>R</i> ,2 <i>R</i>	525

R = Me

R¹

Cl

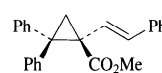
OMe

Cl

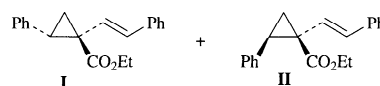
OMe

	ee (%)		abs stereochem		Refs.
	I+II	I:II	I	II	
Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, -78°	(70)	>95:5	>97	—	58
Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, -78°	(41)	>95:5	90	—	58
Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane, rt	(91)	>95:5	89	—	58, 128
Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane, rt	(87)	>95:5	83	—	58, 128

R = Me



Rh ₂ (<i>S</i> -DOSP) ₄ (161a), pentane, 0°	(50)	ee = >98%			500
Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane, 0°	(86)	ee = 97%			500
Rh ₂ (<i>S</i> -biTISP) ₂ (169c), CH ₂ Cl ₂ , rt	(94)	ee = 91%			525
Rh ₂ (<i>S</i> -biTISP) ₂ (169c), CH ₂ Cl ₂ , -50°	(32)	ee = >97%			525

C₁₂ R = Et

	ee (%)		abs stereochem		Refs.
	I+II	I:II	I	II	
Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane, rt	(—)	>95:5	84	—	58, 128
Rh ₂ (<i>S</i> -TBSP) ₄ (161b), CH ₂ Cl ₂ , rt	(—)	>95:5	68	—	58
161e , CH ₂ Cl ₂	(—)	>95:5	68	—	128

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.
C ₁₃	R = <i>i</i> -Pr	Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane, rt	ee (%)		abs stereochem		58, 128		
			I+II	I:II	I	II		I	II
		(—)	>95:5	76	—	1 <i>S</i> ,2 <i>S</i>		—	
C ₁₄	R = <i>t</i> -Bu	Rh ₂ (<i>S</i> -TBSP) ₄ (161b), CH ₂ Cl ₂ , rt	ee (%)		abs stereochem		58		
			I+II	I:II	I	II		I	II
		(—)	>95:5	43	—	1 <i>S</i> ,2 <i>S</i>		—	
C ₁₂	R = menthyl	Rh ₂ (<i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	ee (%)		abs stereochem		309		
			I+II	I:II	I	II		I	II
		(—)	>95:5	43	—	—		—	
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), pentane, rt	ee (%)		abs stereochem		58, 128		
			I+II	I:II	I	II		I	II
		(—)	>95:5	50	—	1 <i>S</i> ,2 <i>S</i>		—	
		Rh ₂ (<i>S</i> -TBSP) ₄ (161b), CH ₂ Cl ₂ , rt	ee (%)		abs stereochem		58		
			I+II	I:II	I	II		I	II
		(38)	>95:5	9	—	1 <i>S</i> ,2 <i>S</i>		—	
		161e , CH ₂ Cl ₂	ee (%)		abs stereochem		128		
			I+II	I:II	I	II		I	II
		(—)	>95:5	9	—	—		—	
		161e , benzene	ee (%)		abs stereochem		128		
			I+II	I:II	I	II		I	II
		(—)	>95:5	28	—	—		—	
		167 , CH ₂ Cl ₂ , rt	ee (%)		abs stereochem		528		
			I+II	I:II	I	II		I	II
		(59)	>95:5	49	—	1 <i>R</i> ,2 <i>R</i>		—	
			ee (%)		abs stereochem		309		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(65)	91:9	25	75	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(62)	80:20	53	82	—		—	
			ee (%)		abs stereochem		109		
			I+II	I:II	I	II		I	II
		(5)	51:49	34	50	—		—	
			ee (%)		abs stereochem		129		
			I+II	I:II	I	II		I	II
		(48)	66:34	37	49	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II
		(26)	70:30	38	26	—		—	
			ee (%)		abs stereochem		108, 109		
			I+II	I:II	I	II		I	II

TABLE VI. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING CHIRAL RHODIUM CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.
R = menthyl									
Menthyl stereochemistry					ee (%)		abs stereochem		
<i>d</i>		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	I+II	I:II	I	II	I	II	309
<i>l</i>		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	(32)	59:41	58	78	—	—	309
<i>d</i>		Rh ₂ (<i>S</i> -PTPI) ₄ (175), CH ₂ Cl ₂ , reflux, 3 h	(59)	61:39	5	9	—	—	519
			(63)	64:36	90	74	—	—	
R = menthyl									
Menthyl stereochemistry					ee (%)				
<i>l</i>		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	(46)	4					309
<i>d</i>		Rh ₂ (<i>S</i> -PTPI) ₄ (175), CH ₂ Cl ₂ , reflux, 3 h	(81)	84					519
C ₁₄									
R = (+)					ee (%)		abs stereochem		
			I+II	I:II	I	II	I	II	
		Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a), CH ₂ Cl ₂ , reflux	(55)	84:16	48	37	—	—	109
		Rh ₂ (5 <i>R</i> -MEPY) ₄ (<i>ent</i> - 171a), CH ₂ Cl ₂ , reflux	(48)	82:18	70	80	—	—	109
C ₁₅									
R = CH(<i>c</i> -C ₆ H ₁₁) ₂					ee (%)		abs stereochem		
			I+II	I:II	I	II	I	II	
		Rh ₂ (<i>S</i> -PTPI) ₄ (175), CH ₂ Cl ₂ , reflux, 3 h	(62)	74:26	43	41	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	522
		Rh ₂ (<i>S</i> -PTPI) ₄ (175), Et ₂ O, reflux, 3 h	(64)	70:30	90	90	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	522
		Rh ₂ (4 <i>S</i> -BNAZ) ₄ (176a), CH ₂ Cl ₂ , rt	(74)	41:59	48	68	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	523
		Rh ₂ (4 <i>S</i> -IBAZ) ₄ (176b), CH ₂ Cl ₂ , rt	(74)	34:66	77	95	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	523

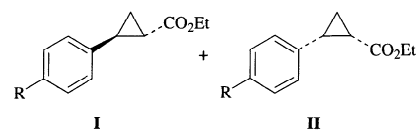
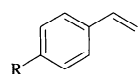
TABLE VII. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING MISCELLANEOUS CHIRAL CATALYSTS

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>(See Chart 5 for Catalyst Structures)</i>				
C₃				
		179, neat, 35°	 (20) ee = 5% (2 <i>S</i>)	530, 88
		179, neat, rt	 (11) ee = 33% (1 <i>S</i> ,2 <i>S</i>)	530
			 I + II	
			ee (%) abs stereochem	
			I+II I:II I II I II	
		179, neat, 0°	(94) 41:59 61 — — —	87
		182g, CH ₂ Cl ₂ , rt, 18 h	(74) 90:10 88 70 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	104
		182g, CH ₂ Cl ₂ , 30°, 10 h	(82) 89:11 92 97 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	531
		193a, CH ₂ Cl ₂ , 30°, 10 h	(79) 89:11 71 48 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	531
		193b, CH ₂ Cl ₂ , 30°, 10 h	(88) 83:17 86 63 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	531
C₄				
		179, neat, 49°	 I + II (13) I:II = —; I ee = —, II ee = —	530
		196, DCE, reflux, 12 h	 I + II (73) I:II = 66:34 I ee = 72% (1 <i>S</i> ,2 <i>S</i>), II ee = 74% (1 <i>S</i> ,2 <i>R</i>)	532
			 I + II	
			ee (%) abs stereochem	
			I+II I:II I II I II	
		179, neat, 10°	(91) 50:50 70 68 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	88
		179, neat, 99°	(95) 57:43 33 16 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	500, 87
		179, neat, rt	(93) 49:51 75 61 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	500
		179, neat, 0°	(92) 46:64 75 67 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	500
		179, neat, -15°	(80) 49:51 76 72 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	500
		179, acetone, 0°	(81) 57:43 — — — —	500
		179, ethyl acetate, 0°	(92) 50:50 — — — —	500
		179, di- <i>n</i> -butyl ether, 0°	(88) 40:60 — — — —	500
		179, <i>n</i> -hexane, 0°	(67) 46:54 — — — —	500
		179, acetophenone, 0°	(95) 49:51 — — — —	500
		180, neat, 35°, 16 h	(50-60) 64:36 20 75 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	85
		182a, CH ₂ Cl ₂ , rt, 18 h	(50) 91:9 82 54 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	106
		182b, CH ₂ Cl ₂ , rt, 18 h	(82) 94:6 91 79 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	106
		182c, CH ₂ Cl ₂ , 30°, 18 h	(66) 90:10 68 24 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	106
		182d, CH ₂ Cl ₂ , 35°, 18 h	(38) 89:11 69 41 1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	106
		<i>ent</i> -182d, CH ₂ Cl ₂ , rt, 10 h	(30) 86:14 76 — 1 <i>R</i> ,2 <i>R</i> —	534
		182e, CH ₂ Cl ₂ , rt, 18 h	(2) 88:12 80 53 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182e, CH ₂ Cl ₂ , 40°, 18 h	(45) 90:10 78 55 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182f, CH ₂ Cl ₂ , rt, 18 h	(29) 92:8 86 70 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182f, CH ₂ Cl ₂ , 40°, 18 h	(66) 90:10 84 68 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182g, CH ₂ Cl ₂ , rt, 18 h	(73) 91:9 89 79 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533, 104, 535
		182g, CH ₂ Cl ₂ , 40°, 18 h	(90) 93:7 89 82 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182h, CH ₂ Cl ₂ , rt, 18 h	(60) 92:8 90 80 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182h, CH ₂ Cl ₂ , 40°, 18 h	(84) 90:10 87 72 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182i, CH ₂ Cl ₂ , rt, 18 h	(74) 91:9 93 87 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533
		182i, CH ₂ Cl ₂ , 40°, 18 h	(81) 90:10 85 68 1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	533

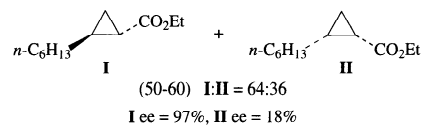
TABLE VII. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING MISCELLANEOUS CHIRAL CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)					Refs.
	184 , CH ₂ Cl ₂ , 5 h	(98)	86:14	—	—	—	536	
	185 , CH ₂ Cl ₂ , rt, 10 h	(51)	91:9	60	—	1 <i>S</i> ,2 <i>S</i>	534	
	186 , CH ₂ Cl ₂ , rt, 10 h	(47)	89:11	41	—	1 <i>R</i> ,2 <i>R</i>	534	
	187 , neat, rt, 5 h	(—)	90:10	14	34	—	84	
	188 , CH ₂ Cl ₂ , rt, 18 h	(83)	95:5	87	4	1 <i>S</i> ,2 <i>S</i>	370	
	188 , CH ₂ Cl ₂ , 0°, 18 h	(63)	96:4	91	4	1 <i>S</i> ,2 <i>S</i>	370	
	188 , DCE, rt	(100)	96:4	87	15	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	83	
	<i>ent</i> - 188 , DCE, rt	(100)	96:4	87	16	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	83	
	188 , DCE, 0°	(100)	95:5	91	27	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	83	
	188 , benzene, rt	(100)	91:9	84	26	1 <i>R</i> ,2 <i>R</i> 1 <i>S</i> ,2 <i>R</i>	83	
	189a , neat, rt	(85)	80:20	46	—	1 <i>R</i> ,2 <i>R</i>	537	
	189a , CH ₂ Cl ₂ , rt, 24 h	(—)	86:14	58	23	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	455	
	189c , CH ₂ Cl ₂ , rt, 24 h	(—)	87:13	15	23	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	455	
	189d , CH ₂ Cl ₂ , rt, 24 h	(—)	70:30	0	11	— 1 <i>S</i> ,2 <i>R</i>	455	
	190a , CH ₂ Cl ₂ , rt, 24 h	(47)	65:35	6	—	1 <i>R</i> ,2 <i>R</i>	538	
	190b , CH ₂ Cl ₂ , rt, 24 h	(32)	65:35	4	—	1 <i>R</i> ,2 <i>R</i>	538	
	190c , CH ₂ Cl ₂ , rt, 24 h	(50)	65:35	8	—	1 <i>R</i> ,2 <i>R</i>	538	
	190d , CH ₂ Cl ₂ , rt, 24 h	(60)	65:35	6	—	1 <i>R</i> ,2 <i>R</i>	538	
	190e , CH ₂ Cl ₂ , rt, 24 h	(49)	65:35	4	—	1 <i>R</i> ,2 <i>R</i>	538	
	190f , CH ₂ Cl ₂ , rt, 24 h	(56)	65:35	3	—	1 <i>R</i> ,2 <i>R</i>	538	
	190g , CH ₂ Cl ₂ , rt, 24 h	(49)	65:35	8	—	1 <i>R</i> ,2 <i>R</i>	538	
	191 , CH ₂ Cl ₂ , rt, 24 h	(63)	65:35	4	—	1 <i>R</i> ,2 <i>R</i>	538	
	193b , CH ₂ Cl ₂ , 30°, 10 h	(93)	89:11	90	66	1 <i>R</i> ,2 <i>R</i> 1 <i>R</i> ,2 <i>S</i>	531	
	194 , CH ₂ Cl ₂ , rt, 24 h	(0)	—	—	—	—	539	
	195 , CH ₂ Cl ₂ , rt, 24 h	(0)	—	—	—	—	539	
	196 , DCE, reflux, 12 h	(71)	68:32	87	79	1 <i>S</i> ,2 <i>S</i> 1 <i>S</i> ,2 <i>R</i>	532	
	197 , CH ₂ Cl ₂ , rt, 24 h	(21)	60:40	14	35	—	539	
	197 , CH ₂ Cl ₂ , -76°, 24 h	(4)	91:9	18	—	—	539	
	197 /AgOTf, CH ₂ Cl ₂ , rt, 24 h	(84)	59:41	17	40	—	539	
	197 /[NEt ₄]Cl, CH ₂ Cl ₂ , rt, 24 h	(15)	60:40	13	32	—	539	

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R		ee (%)		abs stereochem		Refs.	
		I+II	I:II	I	II		I
Cl	179 , neat, 0°	(96)	45:55	—	—	—	87
Me	179 , neat, 0°	(91)	50:50	—	—	—	87
OMe	179 , neat, 0°	(96)	49:51	—	—	—	87
Cl	188 , CH ₂ Cl ₂ , rt, 18 h	(66)	96:4	90	4	—	370
Me	188 , CH ₂ Cl ₂ , rt, 18 h	(78)	95:5	81	9	—	370
OMe	188 , CH ₂ Cl ₂ , rt, 18 h	(61)	94:6	85	8	—	370
F	189a , neat, rt	(92)	92:8	50	—	—	537
Cl	189a , neat, rt	(93)	90:10	52	—	—	537
Br	189a , neat, rt	(93)	86:14	45	—	—	537
Me	189a , neat, rt	(92)	91:9	46	—	—	537
OMe	189a , neat, rt	(>95)	86:14	47	—	—	537



	ee (%)		abs stereochem		Refs.	
	I+II	I:II	I	II		I
179 , neat, 0°	(97)	—	—	—	—	530
188 , CH ₂ Cl ₂ , rt, 18 h	(69)	75:25	87	35	—	370

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TABLE VII. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING MISCELLANEOUS CHIRAL CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																											
		196 , DCE, reflux, 12 h	 I (75) I:II = 72:28 I ee = 89%, II ee = 75%	532																																																																																																											
		196 , DCE, reflux, 12 h	 I (67) I:II = 70:30 I ee = 64% (1 <i>S</i> ,2 <i>S</i>), II ee = 60% (1 <i>S</i> ,2 <i>R</i>)	532																																																																																																											
		179 , neat, 0°	 I (92) I:II = — I ee = 37% (1 <i>R</i> ,2 <i>S</i>), II ee = 71% (1 <i>S</i> ,2 <i>S</i>)	530																																																																																																											
		179 , — 179 , neat, 5° 188 , CH ₂ Cl ₂ , rt, 18 h 196 , DCE, reflux, 12 h	 <table border="1"> <thead> <tr> <th></th> <th>ee (%)</th> <th>abs stereochem</th> </tr> </thead> <tbody> <tr> <td>(70)</td> <td>37</td> <td>1<i>S</i></td> </tr> <tr> <td>(95)</td> <td>70</td> <td>1<i>S</i></td> </tr> <tr> <td>(76)</td> <td>81</td> <td>—</td> </tr> <tr> <td>(65)</td> <td>81</td> <td>1<i>S</i></td> </tr> </tbody> </table>		ee (%)	abs stereochem	(70)	37	1 <i>S</i>	(95)	70	1 <i>S</i>	(76)	81	—	(65)	81	1 <i>S</i>	88 87, 530 370 532																																																																																												
	ee (%)	abs stereochem																																																																																																													
(70)	37	1 <i>S</i>																																																																																																													
(95)	70	1 <i>S</i>																																																																																																													
(76)	81	—																																																																																																													
(65)	81	1 <i>S</i>																																																																																																													
C₅		179 , neat, 0° 193b , CH ₂ Cl ₂ , 30°, 10 h	 I (91) I:II = 53:47; I ee = 84% II (80) I:II = 92:8; I ee = 90% (1 <i>R</i> ,2 <i>R</i>), II ee = 68% (1 <i>R</i> ,2 <i>S</i>)	87 531																																																																																																											
C₆		179 , neat, 0°	 I (94) I:II = 48:52; I ee = 80% II	87																																																																																																											
			 <table border="1"> <thead> <tr> <th rowspan="2">I+II</th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> <th rowspan="2"></th> </tr> <tr> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(0)</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> <td>—</td> </tr> <tr> <td>(76)</td> <td>98:2</td> <td>73</td> <td>—</td> <td>1<i>S</i>,2<i>S</i></td> <td>—</td> </tr> <tr> <td>(85)</td> <td>96:4</td> <td>89</td> <td>93</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(76)</td> <td>95:5</td> <td>75</td> <td>—</td> <td>1<i>S</i>,2<i>S</i></td> <td>—</td> </tr> <tr> <td>(55)</td> <td>94:6</td> <td>83</td> <td>42</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(79)</td> <td>95:5</td> <td>64</td> <td>51</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(69)</td> <td>96:4</td> <td>74</td> <td>—</td> <td>1<i>R</i>,2<i>R</i></td> <td>—</td> </tr> <tr> <td>(83)</td> <td>95:5</td> <td>66</td> <td>82</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(80)</td> <td>96:4</td> <td>93</td> <td>91</td> <td>1<i>S</i>,2<i>S</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> <tr> <td>(65)</td> <td>97:3</td> <td>94</td> <td>87</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>R</i>,2<i>S</i></td> </tr> <tr> <td>(53)</td> <td>67:33</td> <td><10</td> <td><10</td> <td>—</td> <td>—</td> </tr> <tr> <td>(82)</td> <td>93:7</td> <td>68</td> <td>42</td> <td>1<i>R</i>,2<i>R</i></td> <td>1<i>S</i>,2<i>R</i></td> </tr> </tbody> </table>	I+II	ee (%)		abs stereochem			I:II	I	II	I	II	(0)	—	—	—	—	—	(0)	—	—	—	—	—	(0)	—	—	—	—	—	(0)	—	—	—	—	—	(0)	—	—	—	—	—	(76)	98:2	73	—	1 <i>S</i> ,2 <i>S</i>	—	(85)	96:4	89	93	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(76)	95:5	75	—	1 <i>S</i> ,2 <i>S</i>	—	(55)	94:6	83	42	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(79)	95:5	64	51	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(69)	96:4	74	—	1 <i>R</i> ,2 <i>R</i>	—	(83)	95:5	66	82	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(80)	96:4	93	91	1 <i>S</i> ,2 <i>S</i>	1 <i>S</i> ,2 <i>R</i>	(65)	97:3	94	87	1 <i>R</i> ,2 <i>R</i>	1 <i>R</i> ,2 <i>S</i>	(53)	67:33	<10	<10	—	—	(82)	93:7	68	42	1 <i>R</i> ,2 <i>R</i>	1 <i>S</i> ,2 <i>R</i>	540, 541, 542 540 541 540 541, 542 541, 540, 542 540, 542 541, 540, 542 540, 542 540, 541, 542 541 540, 542 540, 542 104 103 531
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TABLE VII. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING MISCELLANEOUS CHIRAL CATALYSTS (Continued)

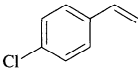
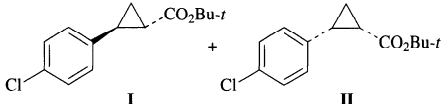
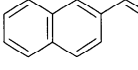
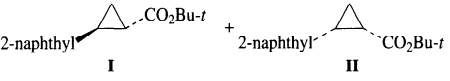
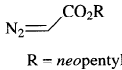
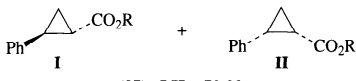
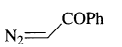
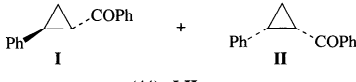
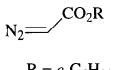
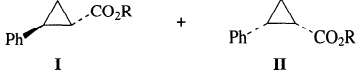
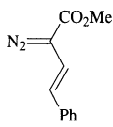
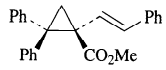
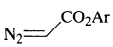
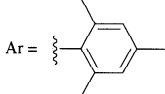

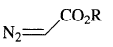
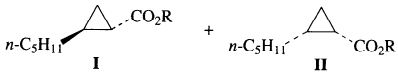

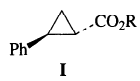
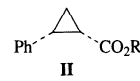
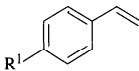
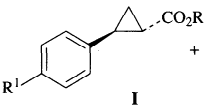
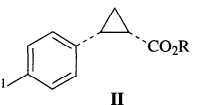

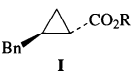
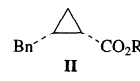

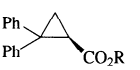
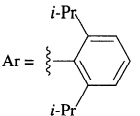

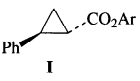
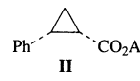
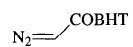
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
		Catalyst, CH ₂ Cl ₂ , rt, 24 h	 <table border="1"> <thead> <tr> <th colspan="2">Catalyst</th> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>ent-181j</td> <td>(67)</td> <td>94:6</td> <td>71</td> <td>—</td> <td>—</td> </tr> <tr> <td>181i</td> <td>(86)</td> <td>97:3</td> <td>96</td> <td>—</td> <td>—</td> </tr> </tbody> </table>	Catalyst		ee (%)		abs stereochem		I+II	I:II	I	II	I	II	ent-181j	(67)	94:6	71	—	—	181i	(86)	97:3	96	—	—	541 540, 542
Catalyst		ee (%)		abs stereochem																								
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Catalyst		ee (%)		abs stereochem																								
I+II	I:II	I	II	I	II																							
ent-181j	(66)	88:12	70	—	—																							
181i	(87)	95:5	92	—	—																							
C₇	 R = neopentyl	Ph-CH=CH ₂ , 179 , neat, 0°	 (87) I:II = 70:30 I ee = 88% (1 <i>S</i> ,2 <i>S</i>), II ee = 81% (1 <i>S</i> ,2 <i>R</i>)	530, 87																								
C₈		Ph-CH=CH ₂ , 179 , neat, 50°	 (44) I:II = — I ee = 20% (1 <i>S</i> ,2 <i>S</i>), II ee = —	530																								
	 R = <i>c</i> -C ₆ H ₁₁	Ph-CH=CH ₂ , 179 , neat, 0°	 (72) I:II = 59:41; I ee = 78%	87																								
C₁₁		Ph-CH=CH-Ph, Catalyst (Chart 2), pentane	 <table border="1"> <thead> <tr> <th>Catalyst</th> <th>Temp</th> <th>ee (%)</th> <th>abs stereochem</th> </tr> </thead> <tbody> <tr> <td>34b/[RuCl₂(C₁₀H₁₄)₂]₂</td> <td>0°</td> <td>(6) >98</td> <td>—</td> </tr> <tr> <td>34b/AgSbF₆</td> <td>rt</td> <td>(2) 24</td> <td>—</td> </tr> <tr> <td>34b/Sc(OTf)₃</td> <td>0°</td> <td>(10) >98</td> <td>—</td> </tr> <tr> <td>34b/Sc(OTf)₃</td> <td>rt</td> <td>(1) >98</td> <td>—</td> </tr> <tr> <td>45c/Sc(OTf)₃</td> <td>0°</td> <td>(9) 86</td> <td>—</td> </tr> </tbody> </table>	Catalyst	Temp	ee (%)	abs stereochem	34b /[RuCl ₂ (C ₁₀ H ₁₄) ₂] ₂	0°	(6) >98	—	34b /AgSbF ₆	rt	(2) 24	—	34b /Sc(OTf) ₃	0°	(10) >98	—	34b /Sc(OTf) ₃	rt	(1) >98	—	45c /Sc(OTf) ₃	0°	(9) 86	—	500
Catalyst	Temp	ee (%)	abs stereochem																									
34b /[RuCl ₂ (C ₁₀ H ₁₄) ₂] ₂	0°	(6) >98	—																									
34b /AgSbF ₆	rt	(2) 24	—																									
34b /Sc(OTf) ₃	0°	(10) >98	—																									
34b /Sc(OTf) ₃	rt	(1) >98	—																									
45c /Sc(OTf) ₃	0°	(9) 86	—																									
	 Ar = 	Ph-CH=CH ₂ , 182g , benzene, 50° 192a , benzene, 50°	 <table border="1"> <thead> <tr> <th colspan="2">ee (%)</th> <th colspan="2">abs stereochem</th> </tr> <tr> <th>I+II</th> <th>I:II</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>182g</td> <td>(95) 98:2</td> <td>93</td> <td>—</td> </tr> <tr> <td>192a</td> <td>(95) 98:2</td> <td>93</td> <td>—</td> </tr> </tbody> </table>	ee (%)		abs stereochem		I+II	I:II	I	II	182g	(95) 98:2	93	—	192a	(95) 98:2	93	—	44								
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I+II	I:II	I	II																									
182g	(95) 98:2	93	—																									
192a	(95) 98:2	93	—																									
C₁₂	 R = <i>l</i> -menthyl	<i>n</i> -C ₅ H ₁₁ -CH=CH ₂ , 182g , CH ₂ Cl ₂ , rt, 18 h	 (54) I:II = 92:8 I ee = 98% (1 <i>R</i> ,2 <i>R</i>), II ee = 94% (1 <i>R</i> ,2 <i>S</i>)	106, 104																								

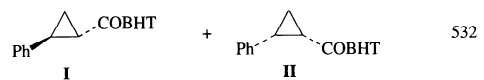
TABLE VII. ASYMMETRIC CYCLOPROPANATION OF ALKENES USING MISCELLANEOUS CHIRAL CATALYSTS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																																																
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C₁₇

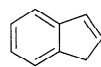


196, DCE, reflux, 12 h

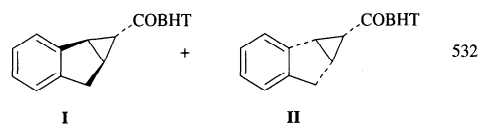


(66) I:II = 93:7

I ee = 87% (1*S*,2*S*), II ee = 84% (1*S*,2*R*)



196, DCE, reflux, 12 h

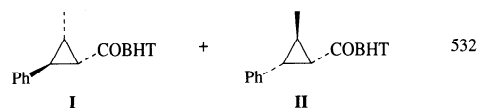


(50) I:II = 98:2

I ee = 95%, II ee = 82%



196, DCE, reflux, 12 h



(51) I:II = 98:2

I ee = 82% (1*S*,2*S*), II ee = 55% (1*S*,2*R*)

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 $N_2=C-CO_2R$				
C_4 R = Et		Catalyst, neat, rt, 8 h		
		Catalyst	I:II	
		$Rh_2(OAc)_4$	(73) 62:38	71, 151
		$Rh_6(CO)_{16}$	(21) 67:33	71, 151
		$CuCl \cdot P(OPr-i)_3$	(17) 72:28	71, 151
		$PdCl_2 \cdot 2PhCN$	(<8) —	71
R = Et		$Rh_2(OAc)_4$, neat, rt, 8 h		71, 543
			(49) I:II = 62:38	
R = Et		Catalyst, neat, rt, 8 h		
			I: R¹ = CO₂Et, R² = H III: R¹ = CO₂Et, R² = H	
			II: R¹ = H, R² = CO₂Et IV: R¹ = H, R² = CO₂Et	
		Catalyst	I:II:III:IV	
		$Rh_2(OAc)_4$	(76) 37:33:17:13	71, 151
		$Rh_6(CO)_{16}$	(80) 37:33:19:11	71, 151
		$CuCl \cdot P(OPr-i)_3$	(33) 48:37:10:5	71, 151
		$PdCl_2 \cdot 2PhCN$	(4) —	71

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (Chart 4), CH ₂ Cl ₂ , rt	 I	287
			 II	
			ee (%)	
		Catalyst	I+II I:II I II	
C ₃	R	Rh ₂ (OAc) ₄	(60) 43:57 — —	
	Me	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(27) 48:52 56 60	
	Me	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(45) 43:57 58 47	
C ₆	<i>t</i> -Bu	Rh ₂ (OAc) ₄	(37) 44:56 — —	
	<i>t</i> -Bu	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(17) 43:57 74 —	
	<i>t</i> -Bu	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(20) 52:48 46 —	
C ₈	Ph	Rh ₂ (OAc) ₄	(77) 42:58 — —	
	Ph	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(38) 51:49 26 —	
	Ph	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(60) 51:49 48 —	
C ₁₂	<i>l</i> -menthyl	Rh ₂ (OAc) ₄	(90) 37:63 — —	
	<i>l</i> -menthyl	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(41) 38:62 72 60	
	<i>l</i> -menthyl	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(31) 49:51 54 52	
C ₁₂	<i>d</i> -menthyl	Rh ₂ (OAc) ₄	(64) 38:62 — —	
	<i>d</i> -menthyl	Rh ₂ (5 <i>S</i> -MEPY) ₄ (171a)	(22) 45:55 76 50	
	<i>d</i> -menthyl	Rh ₂ (4 <i>S</i> -PHOX) ₄ (173)	(29) 43:57 14 8	
	<i>d</i> -menthyl	179 (Chart 5)	(87) — — —	530
	<i>d</i> -menthyl	28a (Chart 2)	(-60) 63:37 97 (<i>S</i>) 97 (<i>S</i>)	69, 118
		Catalyst (Chart 4), neat, rt, 4 or 8 h	 I: R¹ = CO₂R, R² = H	
			 II: R¹ = H, R² = CO₂R	
			 III: R¹ = CO₂R, R² = H	
			 IV: R¹ = H, R² = CO₂R	
		Catalyst	I:II:III:IV	
		Time		
C ₃	R	Rh ₂ (OAc) ₄	(99) 30:32:25:13	544
	Me	168q	(99) 37:26:14:23	544, 71
C ₄	Et	Rh ₂ (OAc) ₄	(93) 28:29:24:12	151, 543, 544, 71
	Et	168q	(98) 37:27:14:22	544
	Et	Rh ₆ (CO) ₁₆	(70) 32:29:25:14	151
	Et	Cu(OTf) ₂	(57) 33:33:22:12	543, 80, 71
	Et	CuCl•P(OPr- <i>i</i>) ₃	(81) 37:28:27:8	71, 151
	Et	CuCl•P(OPh) ₃	(73) 36:30:27:7	71
	Et	Cu-bronze	(20) 35:30:28:7	71
	Et	Cu(acac) ₂	(55) 38:29:25:8	71
	Et	Pd(OAc) ₂	(37) 10:12:46:32	543
	Et	PdCl ₂ •2PhCN	(24) 16:18:33:33	71, 151
C ₆	<i>n</i> -Bu	Rh ₂ (OAc) ₄	(88) 61(I+II):27:12	544
	<i>n</i> -Bu	168q	(99) 62(I+II):17:21	544
	<i>t</i> -Bu	Rh ₂ (OAc) ₄	(85) 27:36:28:9	544
	<i>t</i> -Bu	168q	(95) 9:52:24:15	544
C ₄	Et	Rh ₂ (OPiv) ₄ , rt	(93) 61(I+II):39(III+IV)	80
	Et	179 (Chart 5)	(87) —	530
	Et	(CO) ₅ W=C(OMe)Ph	(25) —	321
	Et	RuCl ₂ (PPh ₃) ₃	(26) 73.5:14.5:8:4	52
	Et	RuCl ₂ (PPh ₃) ₃ /C ₆ H ₆	(25) 74:14:8:4	52
	Et	RuH ₃ [Si(OEt) ₃](PPh ₃) ₂	(19) 78:11.5:7:3.5	52
	Et	Ru[Si(OEt) ₃] ₂ (PPh ₃) ₂	(23) 81:10:6:3	52
C ₆	<i>n</i> -Bu	Pd(OAc) ₂ , rt	(48) 23(I+II):77(III+IV)	80

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.					
C ₁ R = Et		Catalyst, neat, rt, 4 h	 I + II						
					Catalyst	I+II	I:II		
					Rh ₂ (OAc) ₄	(96)	>80:20	543	
					Cu(OTf) ₂	(82)	>80:20	543	
Pd(OAc) ₂	(48)	>75:25	74						
R = Et			 I + II						
						I: R ¹ = CO ₂ Et, R ² = H	III: R ¹ = CO ₂ Et, R ² = H		
						II: R ¹ = H, R ² = CO ₂ Et	IV: R ¹ = H, R ² = CO ₂ Et		
						I+II:III+IV			
					Rh ₂ (OAc) ₄ , neat, rt, 8 h	(61)	54:34:12 (I:II:III+IV)	71, 151	
					Rh ₆ (CO) ₁₆ , neat, rt, 8 h	(72)	89:11	151	
					CuCl•P(OPr- <i>i</i>) ₃ neat, rt, 8 h	(23)	91:9	151	
					PdCl ₂ •2PhCN neat, rt, 8 h	(31)	77:23	151	
					Rh ₂ (OPiv) ₄ , rt	(96)	76:24	80	
					Cu(OTf) ₂ , rt	(82)	80:20	80	
Pd(OPiv) ₂ , rt	(48)	73:27	80						
R = Et			 I + II						
						I: R ² = CO ₂ Et, R ³ = H	III: R ² = CO ₂ Et, R ³ = H		
						II: R ² = H, R ³ = CO ₂ Et	IV: R ² = H, R ³ = CO ₂ Et		
						I:II:III+IV			
					Me	Rh ₂ (OAc) ₄ , neat, rt, 8 h	(90)	52:37:4:7 (I:II:III+IV)	71, 151
					Me	Rh ₆ (CO) ₁₆ , neat, rt, 8 h	(63)	52:40:8	71, 151
					Me	CuCl•P(OPr- <i>i</i>) ₃ neat, rt, 8 h	(57)	56:38:16	71, 151
Me	PdCl ₂ •2PhCN neat, rt, 8 h	(22)	40:33:27	71, 151					
Me	Cu	(—)	—	545					
TMS	Cu	(—)	—	545					

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
			ee (%)		
			I+II I:II I II		
C ₃	R ¹ R ² R ³ R ⁴				
	Me	H H H TMS	120b (Chart 3)	(64) 56:44 58 74	502
	Me	H H H TMS	95a (Chart 3)	(59) 58:42 61 72	502
	Me	H H H TMS	34b (Chart 2)	(72) 55:45 74 >95	458
	Me	H H H TBDMS	Cu(acac) ₂ , EtOAc	(64) 67:33 — —	546
	Me	H Me H TBDMS	34b (Chart 2)	(50) 62:38 69 >95	458
	Me	H Me Me TBDMS	Cu(acac) ₂ , EtOAc	(52) — — —	546
	Me	H Me H TMS	120b (Chart 3)	(53) 58:42 64 67	502
	Me	H Me H TMS	95a (Chart 3)	(27) 56:44 53 62	502
	Me	H H Me TMS	34b (Chart 2)	(28) >90:10 64 —	458
	Me	H H Me TMS	95a (Chart 3)	(35) 64:36 72 72	458
	Me	Me H H TMS	Cu(acac) ₂ , EtOAc	(61) — — —	547
	Me	CH ₂ OTBDMS H H TMS	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(73) — — —	547
	Me	Ph H H TBDMS	Cu(acac) ₂ , EtOAc	(80) 72:28 — —	506
	Me	Ph H H TMS	120b (Chart 3)	(73) 48:52 23 42	502
	Me	Ph H H TMS	95a (Chart 3)	(67) 52:48 56 70	502
	Me	<i>p</i> -(CF ₃) ₂ C ₆ H ₄ H H TBDMS	Cu(acac) ₂ , EtOAc	(84) 72:28 — —	546
	Me	Me H H TBDMS	Cu(acac) ₂ , EtOAc	(76) 65:35 — —	546
	Me	MeO H H TBDMS	Cu(acac) ₂ , EtOAc	(72) 75:25 — —	546
C ₄	Et	H H H Me	Rh ₂ (OAc) ₄ , neat, rt, 8 h	(88) — — —	71, 151
	Et	H H H Me	Rh ₆ (CO) ₁₆ , neat, rt, 8 h	(63) — — —	151
	Et	H H H Me	CuCl•P(OP <i>i</i> -)₃, neat, rt, 8 h	(38) — — —	151
	Et	H H H Me	PdCl ₂ •2PhCN, neat, rt, 8 h	(18) — — —	151
	Et	H H H Me	(CO) ₅ W=C(OMe)Ph	(46) 55:45 — —	321
	Et	H H H TMS	Cu(acac) ₂ , 90°, benzene	(78) — — —	548
	Et	H Me H TMS	Cu(acac) ₂ , 90°, benzene	(68) — — —	548
	Et	H OMe H Me	Rh ₂ (OAc) ₄ , neat, rt, 8 h	(76) 55:45 — —	71
	R = Et				
				I+II I:II	
			Rh ₂ (OAc) ₄ , neat, rt, 4 h	(90) —	543, 77
			Cu(OTf) ₂ , neat, rt, 4 h	(70) —	543, 77
			Pd(OAc) ₂ , neat, rt, 4 h	(20) —	543, 77
			Rh ₂ (OPiv) ₄ , rt	(90) —	80
			Cu(OTf) ₂ , rt	(53) —	80
			Pd(OPiv) ₂ , rt	(18) —	80
			23a (Chart 1)	(69) 67:33	51
			23b (Chart 1)	(37) 60:40	51
			23c (Chart 1)	(75) 67:33	51
	R = Et		Cu		545
		R ¹ = Me, TMS		I (—) II (—)	
C ₃	R = Me		Cu(acac) ₂		(65) 549

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

Carbenoid Precursor		Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.
	<u>R</u>			<u>I+II</u>	<u>I:II</u>	<u>ee (%)</u>		<u>abs stereochem</u>		
				<u>I</u>	<u>II</u>	<u>I</u>	<u>II</u>	<u>I</u>	<u>II</u>	
C ₃	Me		Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -3) ₄ , rt	(69)	44:56	—	—	—	—	544
	Me		Rh ₂ (OAc) ₄ , neat, rt, 4 h	(56)	52:48	—	—	—	—	544
C ₄	Et		Rh ₆ (CO) ₁₆ , neat, rt, 8 h	(77)	—	—	—	—	—	543
	Et		CuCl•P(OPr- <i>i</i>) ₃ neat, rt, 8 h	(35)	—	—	—	—	—	543
	Et		Rh ₂ (TFA) ₄ , neat, rt, 4 h	(29)	52:48	—	—	—	—	544
	Et		Rh ₂ (O ₂ CC ₆ F ₅) ₄ , neat, rt, 8 h	(64)	52:48	—	—	—	—	543
	Et		Rh ₂ (OPiv) ₄ , neat, rt, 8 h	(56)	47:53	—	—	—	—	543
	Et		Rh ₂ [O ₂ C-2,4-Cl ₂ C ₆ H(NO ₂) ₂ -3,5] ₄	(15)	47:53	—	—	—	—	544
	Et		Rh ₂ [O ₂ CC ₆ H ₃ (OMe) ₂ -2,6] ₄ , rt	(68)	50:50	—	—	—	—	544
	Et		168q (Chart 4), neat, rt, 4 h	(58)	45:55	—	—	—	—	544
	Et		Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ -3) ₄ , rt	(86)	42:58	—	—	—	—	544
	Et		Cu	(45)	57:43	—	—	—	—	463
	Et		95a (Chart 3)	(33)	60:40	22	15	1 <i>S</i> ,3 <i>S</i>	1 <i>S</i> ,3 <i>R</i>	463
	Et		94 (Chart 3)	(3)	59:41	5	17	1 <i>R</i> ,3 <i>R</i>	1 <i>S</i> ,3 <i>R</i>	463
	Et		97 (Chart 3)	(15)	58:42	10	29	1 <i>R</i> ,3 <i>R</i>	1 <i>S</i> ,3 <i>R</i>	463
	Et		96 (Chart 3)	(16)	57:43	16	2	1 <i>R</i> ,3 <i>R</i>	1 <i>S</i> ,3 <i>R</i>	463
	Et		151a (Chart 3), 53°	(22)	60:40	17	5	1 <i>S</i> ,3 <i>S</i>	1 <i>R</i> ,3 <i>S</i>	551
	Et		150a (Chart 3), 50°	(44)	58:42	7	5	1 <i>S</i> ,3 <i>S</i>	1 <i>S</i> ,3 <i>R</i>	551
	Et		151b (Chart 3), 50°	(49)	64:36	6	5	1 <i>R</i> ,3 <i>R</i>	1 <i>R</i> ,3 <i>S</i>	551
	Et		150b (Chart 3), 50°	(44)	60:40	3	10	1 <i>S</i> ,3 <i>S</i>	1 <i>R</i> ,3 <i>S</i>	551
	Et		151c (Chart 3), 50°	(17)	56:44	4	9	1 <i>R</i> ,3 <i>R</i>	1 <i>R</i> ,3 <i>S</i>	551
	Et		150c (Chart 3), 50°	(43)	57:43	12	16	1 <i>R</i> ,3 <i>R</i>	1 <i>R</i> ,3 <i>S</i>	551
	Et		Cu-(L-Ala) ₂	(46)	55:45	<3	<3	—	—	336
	Et		NaCuX-zeolite-(L-Ala) ₂	(59)	55:45	<3	<3	—	—	336
	Et		NaCuX-zeolite-(L-Val) ₂	(57)	53:47	<3	<3	—	—	336
	Et		NaCuX-zeolite (L-Pro) ₂	(58)	55:45	<3	<3	—	—	336
	Et		NaCuX-zeolite-[(<i>R</i>)-1,2-propanediamine] ₂	(54)	54:46	<3	<3	—	—	336
C ₆	<i>n</i> -Bu		Rh ₂ (OAc) ₄ , neat, rt, 4 h	(58)	46:54	—	—	—	—	544
	<i>n</i> -Bu		Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ - <i>m</i>) ₄ , rt	(96)	40:60	—	—	—	—	544
	<i>t</i> -Bu		Rh ₂ (OAc) ₄ , neat, rt, 8 h	(56)	44:56	—	—	—	—	543
	<i>t</i> -Bu		Rh ₂ (TFA) ₄ , neat, rt, 8 h	(45)	56:44	—	—	—	—	543
	<i>t</i> -Bu		Rh ₂ (O ₂ CC ₆ F ₅) ₄ , neat, rt, 8 h	(56)	53:47	—	—	—	—	543
	<i>t</i> -Bu		Rh ₂ (OPiv) ₄ , neat, rt, 8 h	(32)	44:56	—	—	—	—	543
C ₈	CH ₂ CH ₂ NEt ₂		Cu powder/CuSO ₄ , 110 °	(16)	—	—	—	—	—	552
	CH ₂ CH ₂ SBu		Cu powder/CuSO ₄ , 110 °	(23)	55:45	—	—	—	—	553
C ₉	2,4-dimethyl-3-pentyl		36a (Chart 2)	(60)	97:3	92	—	—	—	125
C ₁₂	<i>l</i> -menthyl		36a (Chart 2)	(60)	88:12	92	85	—	—	125
C ₁₅	dicyclohexylmethyl		36a (Chart 2)	(62)	99:1	92	—	—	—	125
C ₄	R = Et		Catalyst, neat, rt, 8 h							543
			Catalyst	<u>I+II</u>	<u>I:II</u>					
			Rh ₂ (OAc) ₄	(85)	—					
			Rh ₆ (CO) ₁₆	(76)	—					
			CuCl•P(OPr- <i>i</i>) ₃	(35)	—					
C ₁₂	<u>R</u>		28b (Chart 2)	(77)	<u>I:II</u> = 63:37; <u>I</u> 97% ee (1 <i>S</i>), <u>II</u> 97% ee (1 <i>S</i>)					69
	<i>d</i> -menthyl		182g (Chart 5)	(86)	<u>I:II</u> = 79:21; <u>I</u> 98% ee (1 <i>R</i> ,3 <i>R</i>), <u>II</u> 79% ee (1 <i>R</i> ,3 <i>S</i>)					106

TABLE VIII. REACTION OF CARBENOID WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
C ₄ R = Et		 I + II	<table border="1"> <thead> <tr> <th></th> <th>I+II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Cu</td> <td>(57)</td> <td>57:43</td> </tr> <tr> <td>Rh₂(OAc)₄, rt, 4 h</td> <td>(76)</td> <td>—</td> </tr> <tr> <td>Cu(OTf)₂, rt, 8 h</td> <td>(85)</td> <td>—</td> </tr> <tr> <td>CuCl•P(OPr-<i>i</i>)₃ neat, rt, 8 h</td> <td>(30)</td> <td>—</td> </tr> </tbody> </table>		I+II	I:II	Cu	(57)	57:43	Rh ₂ (OAc) ₄ , rt, 4 h	(76)	—	Cu(OTf) ₂ , rt, 8 h	(85)	—	CuCl•P(OPr- <i>i</i>) ₃ neat, rt, 8 h	(30)	—	150 543 543 543
				I+II	I:II														
			Cu	(57)	57:43														
			Rh ₂ (OAc) ₄ , rt, 4 h	(76)	—														
			Cu(OTf) ₂ , rt, 8 h	(85)	—														
CuCl•P(OPr- <i>i</i>) ₃ neat, rt, 8 h	(30)	—																	
R = Et		 I + II	<table border="1"> <thead> <tr> <th></th> <th>I+II:III+IV</th> </tr> </thead> <tbody> <tr> <td>Cu</td> <td>(51) 41:31:17:10 (I:II:III:IV)</td> </tr> <tr> <td>Rh₂(OAc)₄, neat, rt, 8 h</td> <td>(87) 76:24</td> </tr> <tr> <td>Rh₆(CO)₁₆, neat, rt, 8 h</td> <td>(81) 76:24</td> </tr> <tr> <td>CuCl•P(OPr-<i>i</i>)₃ neat, rt, 8 h</td> <td>(60) 50:50</td> </tr> </tbody> </table>		I+II:III+IV	Cu	(51) 41:31:17:10 (I:II:III:IV)	Rh ₂ (OAc) ₄ , neat, rt, 8 h	(87) 76:24	Rh ₆ (CO) ₁₆ , neat, rt, 8 h	(81) 76:24	CuCl•P(OPr- <i>i</i>) ₃ neat, rt, 8 h	(60) 50:50	150 543 543 543					
				I+II:III+IV															
			Cu	(51) 41:31:17:10 (I:II:III:IV)															
			Rh ₂ (OAc) ₄ , neat, rt, 8 h	(87) 76:24															
			Rh ₆ (CO) ₁₆ , neat, rt, 8 h	(81) 76:24															
CuCl•P(OPr- <i>i</i>) ₃ neat, rt, 8 h	(60) 50:50																		
R = Et		 I + II	<table border="1"> <thead> <tr> <th></th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Cu</td> <td>(59) I:II = 68:32</td> </tr> </tbody> </table>		I:II	Cu	(59) I:II = 68:32	150											
				I:II															
Cu	(59) I:II = 68:32																		
R = Et		 I + II	<table border="1"> <thead> <tr> <th></th> <th>I:II</th> <th>ee (%) I and II</th> </tr> </thead> <tbody> <tr> <td>Cu</td> <td>(17) 49:51</td> <td>0</td> </tr> <tr> <td>95a (Chart 3)</td> <td>(9) 49:51</td> <td>0</td> </tr> <tr> <td>61 (Chart 2)</td> <td>(4) 49:51</td> <td>0</td> </tr> </tbody> </table>		I:II	ee (%) I and II	Cu	(17) 49:51	0	95a (Chart 3)	(9) 49:51	0	61 (Chart 2)	(4) 49:51	0	463			
				I:II	ee (%) I and II														
			Cu	(17) 49:51	0														
			95a (Chart 3)	(9) 49:51	0														
61 (Chart 2)	(4) 49:51	0																	
R = Et		 I + II	<table border="1"> <thead> <tr> <th></th> <th>I+II:III+IV</th> </tr> </thead> <tbody> <tr> <td>Cu</td> <td>(98) I+II:III = 92:8</td> </tr> <tr> <td>Rh₂(OAc)₄</td> <td>(66) I+II:III:IV = 62:40:8</td> </tr> <tr> <td>Cu(OTf)₂</td> <td>(83) I+II:III = 93:7</td> </tr> <tr> <td>Cu(OTf)₂</td> <td>(62) I+II:III:IV = 65:22:3</td> </tr> <tr> <td>Pd(OAc)₂</td> <td>(22) I</td> </tr> </tbody> </table>		I+II:III+IV	Cu	(98) I+II:III = 92:8	Rh ₂ (OAc) ₄	(66) I+II:III:IV = 62:40:8	Cu(OTf) ₂	(83) I+II:III = 93:7	Cu(OTf) ₂	(62) I+II:III:IV = 65:22:3	Pd(OAc) ₂	(22) I	543			
				I+II:III+IV															
			Cu	(98) I+II:III = 92:8															
			Rh ₂ (OAc) ₄	(66) I+II:III:IV = 62:40:8															
			Cu(OTf) ₂	(83) I+II:III = 93:7															
Cu(OTf) ₂	(62) I+II:III:IV = 65:22:3																		
Pd(OAc) ₂	(22) I																		
R = Et		 I + II	<table border="1"> <thead> <tr> <th></th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Cu, 110°, 2 h</td> <td>(57) I:II = —</td> </tr> </tbody> </table>		I:II	Cu, 110°, 2 h	(57) I:II = —	554											
				I:II															
Cu, 110°, 2 h	(57) I:II = —																		
C ₃ R = Me		 I	<table border="1"> <tbody> <tr> <td>Cu, neat, 95-110°, 4 h</td> <td>(37)</td> </tr> <tr> <td>CuSO₄, neat, 95-110°, 2 h</td> <td>(34)</td> </tr> </tbody> </table>	Cu, neat, 95-110°, 4 h	(37)	CuSO ₄ , neat, 95-110°, 2 h	(34)	555 556											
			Cu, neat, 95-110°, 4 h	(37)															
			CuSO ₄ , neat, 95-110°, 2 h	(34)															
C ₄ R = Et		 I	(—)	556															

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)


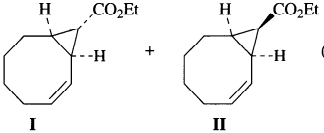
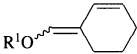
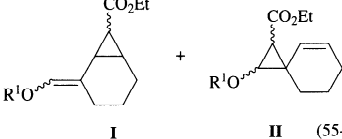
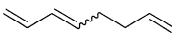
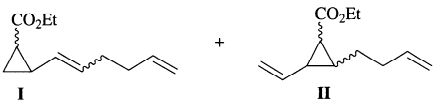

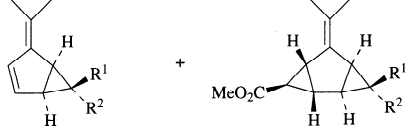

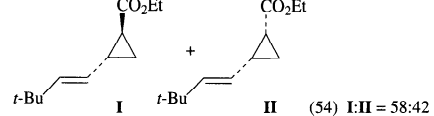

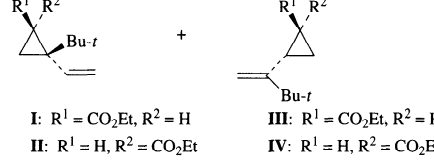
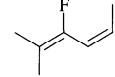
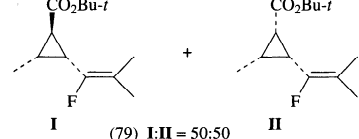
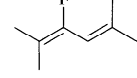
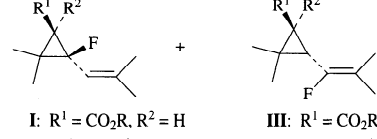
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		CuSO ₄ , 110°	 (51) I:II = —	557
R = Et	 R ¹ = Me, TMS	Cu	 (55-80) I:II = —	545
R = Et		Catalyst, neat, rt, 4 h		543
		Catalyst	I+II	I:II
		Rh ₂ (OAc) ₄	(97)	90:10
		Cu(OTf) ₂	(64)	88:12
		Pd(OAc) ₂	(27)	74:26
C ₃ R = Me		CuCl•P(OPh) ₃ , 45°	 R ¹ = CO ₂ Me, R ² = H (8) R ¹ = H, R ² = CO ₂ Me (67) R ¹ = CO ₂ Me, R ² = H (1.5) R ¹ = H, R ² = CO ₂ Me (6)	558, 559
C ₄ R = Et		Rh ₂ (OAc) ₄ , neat, rt, 8 h	 (54) I:II = 58:42	71
R = Et		Catalyst, neat, rt, 8 h	 I: R ¹ = CO ₂ Et, R ² = H II: R ¹ = H, R ² = CO ₂ Et III: R ¹ = CO ₂ Et, R ² = H IV: R ¹ = H, R ² = CO ₂ Et	71
		Catalyst	I:II:III:IV	
		Rh ₂ (OAc) ₄	(70)	20:16:50:14
		Rh ₆ (CO) ₁₆	(9)	25:20:43:12
		CuCl•P(OPr- <i>i</i>) ₃	(20)	40:20:35:5
		PdCl ₂ •2PhCN	(6)	13:20:45:20
C ₆ R = <i>t</i> -Bu		Rh ₂ (OAc) ₄ , ether, rt	 (79) I:II = 50:50	560
			 I: R ¹ = CO ₂ R, R ² = H II: R ¹ = H, R ² = CO ₂ R III: R ¹ = CO ₂ R, R ² = H IV: R ¹ = H, R ² = CO ₂ R	560
			I:II:III:IV	
C ₃ Me		Rh ₂ (OAc) ₄	(67)	18:38:20:24
Me		CuSO ₄	(—)	—
C ₄ Et		Rh ₂ (OAc) ₄	(—)	—
C ₆ <i>t</i> -Bu		Rh ₂ (OAc) ₄	(54)	20:42:14:24

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

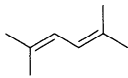
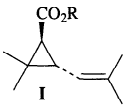
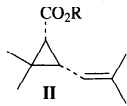
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.
					ee (%)		abs stereochem		
	R		I+II	I:II	I	II	I	II	
C ₃	Me	Rh ₂ (OAc) ₄ , neat, rt, 4 h	(100)	61:39	—	—	—	—	544
	Me	168q (Chart 4), neat, rt, 4 h	(100)	50:50	—	—	—	—	544
C ₄	CH ₂ CN	Cu/CuSO ₄ , 80°	(75)	—	—	—	—	—	349
	CH ₂ CH ₂ Cl	Cu, 115-120°	(53)	55:45	—	—	—	—	341
	CH ₂ CH ₂ Br	Cu/CuSO ₄ , 110°	(50)	—	—	—	—	—	342
	Et	Cu-bronze	(34)	73:27	—	—	—	—	71
	Et	Cu(OiPr) ₂	(93)	70:30	—	—	—	—	71, 77
	Et	Cu(acac) ₂	(76)	64:36	—	—	—	—	71
	Et	Rh ₂ (OAc) ₄ , 60°	(50)	—	—	—	—	—	544, 543, 560
	Et	Rh ₂ (OAc) ₄ , neat, rt, 4 h	(100)	59:41	—	—	—	—	544, 71, 77, 78, 94
	Et	Rh ₂ (acetamide) ₄	(—)	60:40	—	—	—	—	78
	Et	Rh ₂ (TFA) ₄ , neat, rt, 4 h	(85)	60:40	—	—	—	—	544
	Et	Rh ₂ [O ₂ C-2,4-Cl ₂ -3,5-(O ₂ N) ₂ C ₆ H ₃] ₄	(53)	56:44	—	—	—	—	544
	Et	Rh ₂ [O ₂ C-2,6-(MeO) ₂ C ₆ H ₃] ₄ , rt	(92)	57:43	—	—	—	—	544
	Et	168q (Chart 4), neat, rt, 4 h	(99)	49:51	—	—	—	—	544
	Et	Rh ₂ (O ₂ CC ₆ H ₄ CF ₃ - <i>m</i>) ₄ , rt	(100)	57:43	—	—	—	—	544
	Et	Rh ₂ (CO) ₁₆ , neat, rt, 8 h	(87)	69:31	—	—	—	—	71, 318, 543
	Et	CuCl•P(OPr- <i>i</i>) ₃ , rt, 8 h	(55)	73:27	—	—	—	—	71, 77, 318, 543
	Et	CuCl•P(OPh) ₃ , rt, 8 h	(66)	73:27	—	—	—	—	71
	Et	Rh ₂ (O ₂ C-polyethylene) ₄	(56)	70:30	—	—	—	—	367
	Et	PdCl ₂ •2PhCN	(20)	70:30	—	—	—	—	71, 318
Et	Pd(OAc) ₂	(35)	—	—	—	—	—	77	
Et	CuSO ₄	(—)	61:39	—	—	—	—	569, 561	
C ₆	Et	23a (Chart 1)	(96)	58:42	—	—	—	—	51
	Et	23b (Chart 1)	(61)	60:40	—	—	—	—	51
	Et	23c (Chart 1)	(97)	56:44	—	—	—	—	51
	Et	130a (Chart 3), 5°	(64)	55:45	~8	—	—	—	562
	Et	130b (Chart 3), 5°	(74)	57:43	~10	—	—	—	562
	Et	130c (Chart 3), 5°	(71)	55:45	~1	—	—	—	562
	Et	91e (Chart 3), neat, 20°	(54)	51:49	68	62	1 <i>S</i> ,3 <i>S</i>	1 <i>S</i> ,3 <i>R</i>	112
	Et	91a (Chart 3), neat, 40°, 5 h	(64)	62:38	—	—	—	—	41
	Et	91b (Chart 3), neat, 40°, 5 h	(60)	59:41	—	—	—	—	41
	Et	91c (Chart 3), neat, 40°, 5 h	(54)	58:42	—	—	—	—	41
	Et	<i>ent</i> - 91f (Chart 3), neat, 40°, 5 h	(58)	62:38	—	—	—	—	41
	Et	<i>ent</i> - 91g (Chart 3), neat, 40°, 5 h	(53)	58:42	—	—	—	—	41
	Et	<i>ent</i> - 91h (Chart 3), neat, 40°, 5 h	(52)	57:43	—	—	—	—	41
	Et	91i (Chart 3), neat, 40°, 5 h	(59)	60:40	—	—	—	—	41
	Et	91j (Chart 3), neat, 40°, 5 h	(46)	58:42	—	—	—	—	41
Et	91k (Chart 3), neat, 40°, 5 h	(51)	67:33	—	—	—	—	41	
C ₆	<i>n</i> -Bu	Rh ₂ (OAc) ₄ , neat, rt, 4 h	(100)	57:43	—	—	—	—	544
	<i>n</i> -Bu	168q (Chart 4), neat, rt, 4 h	(97)	45:55	—	—	—	—	544
	<i>t</i> -Bu	Rh ₂ (OAc) ₄ , neat, rt, 4 h	(100)	64:36	—	—	—	—	544
	<i>t</i> -Bu	168q (Chart 4), neat, rt, 4 h	(99)	44:56	—	—	—	—	544
C ₈	cyclohexyl	91e (Chart 3), neat, 20°	(71)	75:25	75	46	1 <i>S</i> ,3 <i>S</i>	1 <i>S</i> ,3 <i>R</i>	112
	CH ₂ CH ₂ SBu- <i>n</i>	Cu/CuSO ₄ , 110°	(40)	55:45	—	—	—	—	553
	CH ₂ CH ₂ NEt ₂	Cu/CuSO ₄ , 110°	(23)	55:45	—	—	—	—	552
C ₉	2,3-Me ₂ -2-butyl	91e (Chart 3), neat, 20°	(71)	78:22	85	43	1 <i>S</i> ,3 <i>S</i>	1 <i>S</i> ,3 <i>R</i>	112
	2,3-Me ₂ -2-pentyl	36a (see Chart 2), 0°- rt	(78)	93:7	94	—	1 <i>R</i> ,3 <i>R</i>	—	125
	2,3-Me ₂ -2-pentyl	Rh ₂ (OAc) ₄ , rt, 7 h	(88)	65:35	—	—	—	—	78
C ₁₀	2,3,4-Me ₂ -3-pentyl	Rh ₂ (acetamide) ₄ , rt, 7 h	(95)	59:41	—	—	—	—	78
	2,3,4-Me ₂ -3-pentyl	91e (Chart 3), neat, 20°	(64)	92:8	88	—	1 <i>S</i> ,3 <i>S</i>	—	112
	2,3,4-Me ₂ -3-pentyl	36a (Chart 2), 0°- rt	(76)	85:15	88	—	1 <i>R</i> ,3 <i>R</i>	—	125
C ₁₁	α,α-Me ₂ -benzoyl	91e (Chart 3), neat, 20°	(60)	56:44	71	—	1 <i>S</i> ,3 <i>S</i>	—	112
	2-Me-3-(<i>i</i> -Pr)-3-heptyl	Rh ₂ (OAc) ₄ , rt, 7 h	(73)	60:40	—	—	—	—	78
	2-Me-3-(<i>i</i> -Pr)-3-heptyl	Rh ₂ (acetamide) ₄ , rt, 7 h	(62)	60:40	—	—	—	—	78
C ₁₂	<i>l</i> -adamantyl	91e (Chart 3), neat, 20°	(82)	84:16	85	46	1 <i>S</i> ,3 <i>S</i>	1 <i>S</i> ,3 <i>R</i>	112
	<i>d</i> -neomenthyl	91e (Chart 3), neat, 20°	(77)	89:11	87	—	1 <i>S</i> ,3 <i>S</i>	—	112

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)


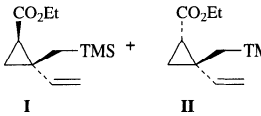
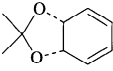
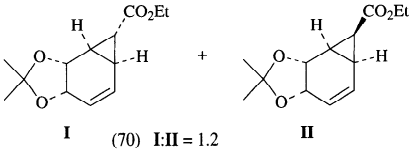

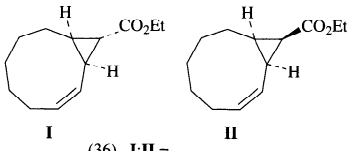
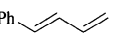
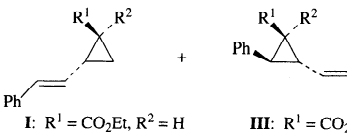

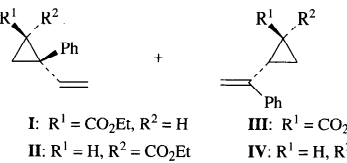
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>d</i> -menthyl		91e (Chart 3), neat, 20°	(64) 72:28 90 59 1 <i>S</i> ,3 <i>S</i> 1 <i>S</i> ,3 <i>R</i>	112
<i>d</i> -menthyl		91e (Chart 3), neat, 20°	(67) 81:19 90 75 1 <i>S</i> ,3 <i>S</i> 1 <i>S</i> ,3 <i>R</i>	112
<i>l</i> -menthyl		91d (Chart 3), neat, 20°	(67) 89:11 87 25 1 <i>S</i> ,3 <i>S</i> 1 <i>S</i> ,3 <i>R</i>	112
<i>l</i> -menthyl		91h (Chart 3), neat, 20°	(42) 91:9 86 22 1 <i>S</i> ,3 <i>S</i> 1 <i>S</i> ,3 <i>R</i>	112
<i>l</i> -menthyl		Cu powder	(69) 76:24 0.7 0 — —	112
<i>l</i> -menthyl		31b (Chart 2), CH ₂ Cl ₂ , 0°- rt	(61) 84:16 24 16 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>l</i> -menthyl		34b (Chart 2), CH ₂ Cl ₂ , 0°- rt	(60) 84:16 24 20 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>l</i> -menthyl		37 (Chart 2), CH ₂ Cl ₂ , 0°- rt	(60) 88:12 40 25 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>l</i> -menthyl		36b (Chart 2), CH ₂ Cl ₂ , 0°- rt	(68) 90:10 72 60 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>l</i> -menthyl		36c (Chart 2), CH ₂ Cl ₂ , 0°- rt	(65) 90:10 82 65 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>l</i> -menthyl		37 (Chart 2), CH ₂ Cl ₂ , 0°- rt	(58) 80:20 90 80 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>d</i> -menthyl		36a (Chart 2), CH ₂ Cl ₂ , 0°- rt	(70) 86:14 90 78 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>l</i> -menthyl		36a (Chart 2), CH ₂ Cl ₂ , 0°- rt	(72) 92:8 92 84 1 <i>R</i> ,3 <i>R</i> 1 <i>R</i> ,3 <i>S</i>	125
<i>l</i> -menthyl		66 (Chart 2), C ₂ H ₄ Cl ₂ , 0°	(47) 88:12 74 — 1 <i>R</i> ,3 <i>R</i> —	483
C ₁₅	dicyclohexylmethyl	36a (Chart 2), CH ₂ Cl ₂ , 0°- rt	(78) 95:5 94 — 1 <i>R</i> ,3 <i>R</i> —	125
	2,6- <i>t</i> -Bu ₂ -4-MeC ₆ H ₂	Rh ₂ (OAc) ₄ , rt, 7 h	(80) 94:6 — — — —	78
	2,6- <i>t</i> -Bu ₂ -4-MeC ₆ H ₂	Rh ₂ (acetamide) ₄ , rt, 7 h	(75) 98:2 — — — —	78
C ₁₇	2,6- <i>t</i> -Bu ₂ -4-MeC ₆ H ₂	37 (Chart 2), CH ₂ Cl ₂ , 0°- rt	(60) 92:8 92 — 1 <i>R</i> ,3 <i>R</i> —	125
	2,6- <i>t</i> -Bu ₂ -4-MeC ₆ H ₂	36a (Chart 2), CH ₂ Cl ₂ , 0°- rt	(75) 94:6 94 — 1 <i>R</i> ,3 <i>R</i> —	125
C ₄	R = Et	 Cu(acac) ₂ , benzene	 (53) I:II = —	563
	R = Et	 Rh ₂ (OAc) ₄ , Et ₂ O, rt, 4 h	 (70) I:II = 1.2	564, 565
	R = Et	 CuSO ₄ , 110°	 (36) I:II = —	557
	R = Et	 Rh ₂ (OAc) ₄ , neat, rt, 8 h Rh ₆ (CO) ₁₆ , neat, rt, 8 h CuCl•P(OPr- <i>i</i>) ₃ , neat, rt, 8 h PdCl ₂ •2PhCN, neat, rt, 8 h 48d (Chart 2) 179 (Chart 5) 75 (Chart 4)	 I: R ¹ = CO ₂ Et, R ² = H III: R ¹ = CO ₂ Et, R ² = H II: R ¹ = H, R ² = CO ₂ Et IV: R ¹ = H, R ² = CO ₂ Et (84) I:II:III:IV = 60:38:1.2:0.8 (40) I+II:III+IV = 98:2 (56) I+II:III+IV = 99:1 (13) I+II:III+IV = 95:5 (90) I:II = 70:30; I ee = 83%, II ee = 89% (72) I+II; I ee = —%, II ee = —% (55) I:II = 48:52; I ee = 96% (1 <i>S</i> ,2 <i>S</i>), II ee = 98% (1 <i>S</i> ,2 <i>R</i>)	71, 151 151 151 151 498 530 522
	R = Et	 Rh ₂ (OAc) ₄ , neat, rt, 8 h Rh ₆ (CO) ₁₆ , neat, rt, 8 h CuCl•P(OPr- <i>i</i>) ₃ , neat, rt, 8 h PdCl ₂ •2PhCN, neat, rt, 8 h Cu ₂ (OTf) ₂ Cu bronze Cu ₂ (acac) ₂	 I: R ¹ = CO ₂ Et, R ² = H III: R ¹ = CO ₂ Et, R ² = H II: R ¹ = H, R ² = CO ₂ Et IV: R ¹ = H, R ² = CO ₂ Et (81) I+II:III:IV = 69:18:13 (71) I+II:III:IV = 72:18:10 (28) I:II:III:IV = 39:36:19:6 (<10) I+II:III:IV = 50:29:21 (48) I:II:III:IV = 35:35:18:12 (30) I:II:III:IV = 40:33:20:7 (42) I:II:III:IV = 37:37:19:7	71, 151 71, 151 71, 151 71, 151 71 71 71

TABLE VIII. REACTION OF CARBENOID WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et		CuBr	(70)	558
R = Et		Catalyst, neat, rt, 4 h	 I: R ¹ = H, R ² = CO ₂ Et II: R ¹ = CO ₂ Et, R ² = H III: R ¹ = H, R ² = CO ₂ Et IV: R ¹ = CO ₂ Et, R ² = H I:II:III:IV (72) 30:28:21:21 (38) 30:30:25:15 (17) 31:31:23:15	543
R = Et		Catalyst, neat, rt, 4 h	 I: R ¹ = CO ₂ Et, R ² = H II: R ¹ = H, R ² = CO ₂ Et III: R ¹ = CO ₂ Et, R ² = H IV: R ¹ = H, R ² = CO ₂ Et I:II:III:IV (50) 27:13:30:30 (87) 26:19:29:26 (72) 25:18:32:35 (33) 42:33:16:9	566 543 543 543
R = Et		CuSO ₄	(50)	566
		Rh ₂ (OAc) ₄ , neat, rt, 4 h	(87)	543
		Cu(OTf) ₂ , neat, rt, 4 h	(72)	543
		Pd(OAc) ₂ , neat, rt, 4 h	(33)	543
R = Et		CuSO ₄ , 100°	(50)	396
R = Et		CuSO ₄ , 100°	(-)	396
R = Et		CuSO ₄ , 70-80°	(50)	398
		Cu	 I (-) I:II = - II	545
C ₃ R = Me	R ¹ = Me, TMS			
R = Me		Cu	(50)	558
R = Me		Cu	 I (-) I:II = - II	545
R = Me	R ¹ = Me, TMS			
R = Me		Cu	 I (-) I:II = - II	545
R = Me	R ¹ = Ac, TMS			

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ R = <i>t</i> -Bu		CuSO ₄ , hexane, 45 °	 I + II (43)	567
R = <i>t</i> -Bu		CuSO ₄ , hexane, 45 °	 I + II (43)	567
	$\frac{R^1}{\text{Me}}$		I (42)	II+III (0)
	Et		I (41)	II+III (15)
C ₈ R = Ph		Cu		558
C ₈ R = C ₆ H ₁₃		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	 I + II (83); I:II -67:33	568
C ₅ R = Et		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	 (35) (26) (4)	568
C ₇ R = <i>t</i> -Bu		Rh ₂ (OAc) ₄		569
C ₄ R = Me		Rh ₂ (OAc) ₄		420
R = Me		Rh ₂ (OAc) ₄		420
R = Me		Rh ₂ (OAc) ₄		420
C ₅ R = Me		Rh ₂ (OAc) ₄		152
C ₇ R = Et		CuSO ₄		570
C ₅ R = Me		Rh ₂ (OAc) ₄		571

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Me		Rh ₂ (OAc) ₄	(31)	53
R = Me		Rh ₂ (OAc) ₄	(35)	53
R = Me		Rh ₂ (OAc) ₄	(43)	53
C ₁₁ R ¹ = OMe, R ² = Ph		Rh ₂ (S-DOSP) ₄ (161a , Chart 4), pentane, -78°	(69) 82% ee	157
C ₉ R ¹ = OEt, R ² = CO ₂ Et		1. Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ 2. Kugelrohr	(50)	156
C ₁₂ R ¹ = OEt, R ² = SO ₂ Ph			(67)	
C ₁₁ R ¹ = OMe, R ² = Ph		Rh ₂ (S-TBSP) ₄ (161b , Chart 4), pentane, rt Rh ₂ (S-DOSP) ₄ (161a , Chart 4), pentane, -78°	(67) ee = 85% (47) ee = 93%	572 157
C ₅ R ¹ = OMe, R ² = H, R ³ = H		Rh ₂ (OPiv) ₄ , pentane	(67)	63
C ₈ R ¹ = OFt, R ² = CH=CH ₂ , R ³ = H		Rh ₂ (OPiv) ₄ , pentane	(89)	
C ₈ R ¹ = O <i>Bu-t</i> , R ² = H, R ³ = H		Rh ₂ (OPiv) ₄ , pentane	(74)	
C ₉ R ¹ = OEt, R ² = CO ₂ Et, R ³ = H		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(87)	
C ₁₁ R ¹ = OEt, R ² = CO ₂ Et, R ³ = OEt		Rh ₂ (OPiv) ₄ , pentane	(79)	
C ₁₁ R ¹ = Me, R ² = Ph, R ³ = H		Rh ₂ (OPiv) ₄ , pentane	(71)	
C ₁₁ R ¹ = OMe, R ² = Ph, R ³ = H		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(73)	
C ₁₂ R ¹ = OEt, R ² = SO ₂ Ph, R ³ = H		Rh ₂ (OPiv) ₄ , pentane	(79)	
C ₁₄ R ¹ = OEt, R ² = CH=CHPh, R ³ = H		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(89)	
C ₉ R ¹ = OEt, R ² = CO ₂ Et, R ³ = OMe		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(18) + (50)	63
C ₁₁ R ¹ = Me, R ² = Ph, R ³ = H		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(35)	63

TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																							
C ₁₂ R ¹ = OEt R ² = SO ₂ Ph R ³ = H		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	 (23) + (47)	63																							
			 (64)	64																							
	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>C₆</td> <td>OMe</td> <td>Me</td> <td>H</td> </tr> <tr> <td>C₈</td> <td>OBu-<i>t</i></td> <td>H</td> <td>H</td> </tr> <tr> <td>C₈</td> <td>OEt</td> <td>CO₂Et</td> <td>H</td> </tr> <tr> <td>C₁₂</td> <td>OEt</td> <td>SPh</td> <td>H</td> </tr> <tr> <td>C₁₄</td> <td>OBu-<i>t</i></td> <td>Ph</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	C ₆	OMe	Me	H	C ₈	OBu- <i>t</i>	H	H	C ₈	OEt	CO ₂ Et	H	C ₁₂	OEt	SPh	H	C ₁₄	OBu- <i>t</i>	Ph	H	Rh ₂ (OOct) ₄ , hexane Rh ₂ (OPiv) ₄ , hexane Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ Rh ₂ (OPiv) ₄ , hexane Rh ₂ (OAc) ₄ , CH ₂ Cl ₂	(>67) (60) (91) (>46) (91)	
R ¹	R ²	R ³																									
C ₆	OMe	Me	H																								
C ₈	OBu- <i>t</i>	H	H																								
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C ₁₄	OBu- <i>t</i>	Ph	H																								
C ₅ R ¹ = OMe R ² = H R ³ = OMe		1. Rh ₂ (OPiv) ₄ , hexane 2. DDQ•TsOH	 (32)	64																							
		1. Rh ₂ (OPiv) ₄ , hexane 2. DDQ•TsOH	 (58)	64																							
	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>C₅</td> <td>OMe</td> <td>Me</td> <td>H</td> </tr> <tr> <td>C₈</td> <td>OMe</td> <td>SEt</td> <td>H</td> </tr> <tr> <td>C₁₁</td> <td>OMe</td> <td>Ph</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	C ₅	OMe	Me	H	C ₈	OMe	SEt	H	C ₁₁	OMe	Ph	H		(39) (64)									
R ¹	R ²	R ³																									
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C ₈	OMe	SEt	H																								
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TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

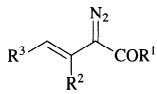

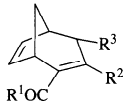
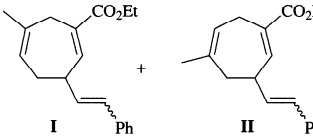
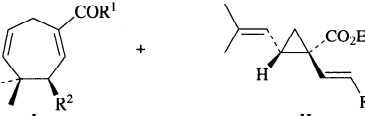
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TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

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$\begin{array}{c} \text{CO}_2\text{Me} \\ \\ \text{N}_2 \\ \\ \text{C}=\text{C} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	$\begin{array}{c} \text{R}^1 \\ \\ \text{C}=\text{C} \\ \quad \\ \text{R}^2 \end{array}$ <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>OAc</td> </tr> <tr> <td>H</td> <td>OTMS</td> </tr> <tr> <td>OTMS</td> <td>H</td> </tr> <tr> <td>OTBDMS</td> <td>H</td> </tr> <tr> <td>OTMS</td> <td>OMe</td> </tr> </tbody> </table>	R ¹	R ²	H	OAc	H	OTMS	OTMS	H	OTBDMS	H	OTMS	OMe	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 40°	 (67) (86) (53) (94) (59)	576	
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TABLE VIII. REACTION OF CARBENOIDS WITH DIENES (Continued)

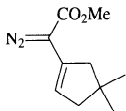
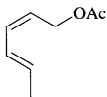
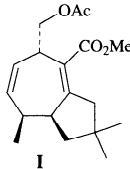
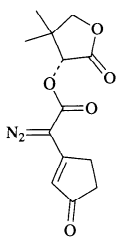

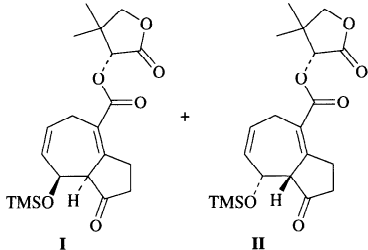
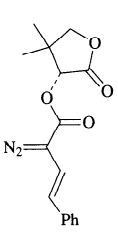

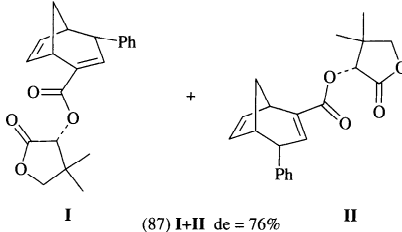
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																										
C₁₀ 		1. Rh ₂ (OOAc) ₄ , hexane, reflux 2. Kugelrohr	 (49)	158																										
		1. Rh ₂ (<i>S</i> -DOSP) ₄ (161a , Chart 4), hexane, reflux 2. Kugelrohr	I (–) ee = 4%	158																										
C₁₃ 		Catalyst, CH ₂ Cl ₂	 I II	148																										
		<table border="1"> <thead> <tr> <th>Catalyst</th> <th>Temp</th> <th>I+II</th> <th>de (%)</th> </tr> </thead> <tbody> <tr> <td>Rh₂(OAc)₄</td> <td>40°</td> <td>(60)</td> <td>91</td> </tr> <tr> <td>Rh₂(OPiv)₄</td> <td>0°</td> <td>(63)</td> <td>69</td> </tr> <tr> <td>Rh₂(OHex)₄</td> <td>0°</td> <td>(58)</td> <td>>90</td> </tr> <tr> <td>Rh₂(OHex)₄</td> <td>40°</td> <td>(80)</td> <td>>90</td> </tr> <tr> <td>Rh₂[(–)-mandelate]₄</td> <td>40°</td> <td>(60)</td> <td>38</td> </tr> <tr> <td>Rh₂[(+)-mandelate]₄</td> <td>40°</td> <td>(56)</td> <td>4</td> </tr> </tbody> </table>	Catalyst	Temp	I+II	de (%)	Rh ₂ (OAc) ₄	40°	(60)	91	Rh ₂ (OPiv) ₄	0°	(63)	69	Rh ₂ (OHex) ₄	0°	(58)	>90	Rh ₂ (OHex) ₄	40°	(80)	>90	Rh ₂ [(–)-mandelate] ₄	40°	(60)	38	Rh ₂ [(+)-mandelate] ₄	40°	(56)	4
Catalyst	Temp	I+II	de (%)																											
Rh ₂ (OAc) ₄	40°	(60)	91																											
Rh ₂ (OPiv) ₄	0°	(63)	69																											
Rh ₂ (OHex) ₄	0°	(58)	>90																											
Rh ₂ (OHex) ₄	40°	(80)	>90																											
Rh ₂ [(–)-mandelate] ₄	40°	(60)	38																											
Rh ₂ [(+)-mandelate] ₄	40°	(56)	4																											
C₁₆ 		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 40°	 I II (87) I+II de = 76%	148																										

TABLE IX. REACTION OF CARBENOIDS WITH FURANS

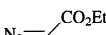

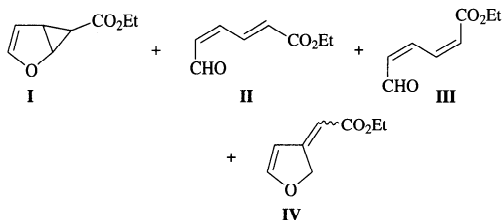
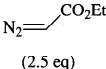
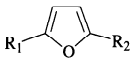
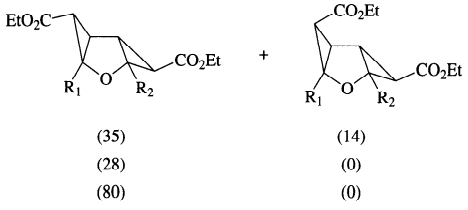
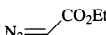

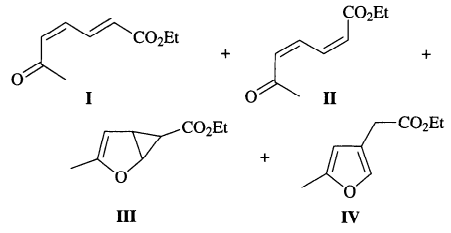

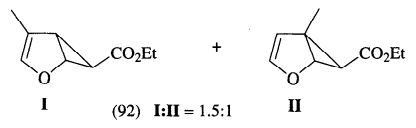

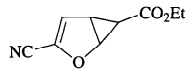

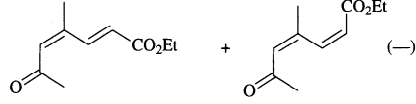
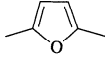
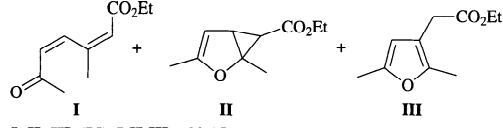
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.														
		Rh ₂ (OAc) ₄ Rh ₂ (OAc) ₄ , neat, rt, 18 h Rh ₂ (OAc) ₄ , neat, 0°, 1 h CuSO ₄ , neat, rt, 2 h CuSO ₄ , neat, 80°, 2 h Cu(acac) ₂ , neat, 0°, 24 h		(65) I:II:III:IV = 18:10:4:1 (66) I:II:III:IV = 17:10:5:1 (—) I:II:III = 6:1:1 (22) I , (30) II+III (5) I , (53) II+III (—) I:II:III = 6:1:1	172 173 161 162 162 161													
					Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 3 h		(35) (28) (80)	(14) (0) (0)	577									
						<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> </tr> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>Me</td> </tr> </table>		R ¹	R ²	H	H	Me	H	Me	Me			
						R ¹	R ²											
						H	H											
			Me	H														
			Me	Me														
		Rh ₂ (OAc) ₄ Rh ₂ (OAc) ₄ , neat, rt, 18 h		(62) I:II:III:IV = 19:6:5:1 (54) I:II:III:IV = 31:12:10:1	172 173													
				Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 10 h		(92) I:II = 1.5:1	171											
		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 10 h		(12-17)	578													
		1. Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 10 h 2. I ₂		(—)	171													
		Rh ₂ (OAc) ₄ Rh ₂ (OAc) ₄ , neat, rt, 18 h CuSO ₄ , neat, 80°, 2 h 1. Cu-Bronze, neat, 91°, 4 h 2. Silica gel 1. Cu-Bronze, neat, 91°, 3 h 2. Alumina		I+II+III (75) I:II:III = 22:15:1 I+II+III (78) I:II:III = 9:6:1 I (72) I (38); III (6) II (36)	172 173 162 160 160													

TABLE IX. REACTION OF CARBENOIDS WITH FURANS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
			 <table border="1"> <thead> <tr> <th></th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>R</td> <td></td> <td></td> </tr> <tr> <td>Me</td> <td>(—)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>(55)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>(0)</td> <td>(36)</td> </tr> <tr> <td>Et</td> <td>(22)</td> <td>(0)</td> </tr> </tbody> </table>		I	II	R			Me	(—)	(0)	Me	(55)	(0)	Me	(0)	(36)	Et	(22)	(0)	172 173 162 578																		
	I	II																																						
R																																								
Me	(—)	(0)																																						
Me	(55)	(0)																																						
Me	(0)	(36)																																						
Et	(22)	(0)																																						
		$\text{Rh}_2(\text{OAc})_4$ $\text{Rh}_2(\text{OAc})_4, \text{CH}_2\text{Cl}_2, \text{rt}, 15 \text{ h}$	(—) (51)	172 173																																				
	$\text{CuSO}_4, 50-70^\circ$		 <table border="1"> <thead> <tr> <th></th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>R¹</td> <td></td> <td></td> </tr> <tr> <td>R²</td> <td></td> <td></td> </tr> <tr> <td>R³</td> <td></td> <td></td> </tr> <tr> <td>R⁴</td> <td></td> <td></td> </tr> <tr> <td>Me</td> <td>(29)</td> <td>(47)</td> </tr> <tr> <td>Me</td> <td>(26)</td> <td>(46)</td> </tr> <tr> <td>H</td> <td>(52)</td> <td>(5)</td> </tr> <tr> <td>H</td> <td>(68)</td> <td>(5)</td> </tr> <tr> <td>H</td> <td>(36)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>(22)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>(—)</td> <td>(58)</td> </tr> </tbody> </table>		I	II	R ¹			R ²			R ³			R ⁴			Me	(29)	(47)	Me	(26)	(46)	H	(52)	(5)	H	(68)	(5)	H	(36)	(0)	H	(22)	(0)	Me	(—)	(58)	174, 330
	I	II																																						
R ¹																																								
R ²																																								
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Me	(29)	(47)																																						
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H	(36)	(0)																																						
H	(22)	(0)																																						
Me	(—)	(58)																																						
		1. $\text{Rh}_2(\text{OAc})_4, \text{CH}_2\text{Cl}_2, \text{rt}, 12 \text{ h}$ 2. $\text{I}_2, \text{CH}_2\text{Cl}_2, \text{rt}, 18 \text{ h}$	 (40)	54																																				
		$\text{Rh}_2(\text{OAc})_4, \text{CH}_2\text{Cl}_2, \text{rt}, 1 \text{ h}$	 (40)	161																																				
		$\text{Rh}_2(\text{OAc})_4, \text{CH}_2\text{Cl}_2, \text{rt}, 3 \text{ h}$	 (76)	577																																				
		1. $\text{Rh}_2(\text{OAc})_4, \text{CH}_2\text{Cl}_2, \text{rt}, 26 \text{ h}$ 2. $\text{I}_2, \text{rt}, 1 \text{ h}$	 (52)	173																																				
		CuSO_4	 (37)	162																																				
		$\text{Rh}_2(\text{OAc})_4$	 (—) I:II = 1.5:1	172																																				
		1. $\text{Rh}_2(\text{OAc})_4$ 2. Silica gel	I (60)	172, 173																																				

TABLE IX. REACTION OF CARBENOIDS WITH FURANS (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
			 +		
C ₅ R = Me		Rh ₂ (OOct) ₄ , hexane, reflux, 1 h Rh ₂ (S-TBSP) ₄ (161b , Chart 4), hexane, reflux, 1 h	(±)- I (51) + II (10-15) (1S,5S)- I (64) ee = 80% + II (15-20)	177 177	
C ₉ R =		Rh ₂ (OOct) ₄ , hexane, reflux, 1 h Rh ₂ (S-TBSP) ₄ (161b , Chart 4), hexane, reflux, 1 h Rh ₂ (R-TBSP) ₄ (<i>ent</i> - 161b , Chart 4), I (44) dc = 0% hexane, reflux, 1 h	I (63) de = 57% I (51) de = 68% I (44) dc = 0%	177 177 177	
C ₅ R = Me		Rh ₂ (OOct) ₄ , hexane, reflux, 1 h Rh ₂ (S-TBSP) ₄ (161b , Chart 4), hexane, reflux, 1 h	(±)- I (90) (1S,5S)- I (94) ee = 46%	177 177	
C ₉ R =		Rh ₂ (OOct) ₄ , hexane, reflux, 1 h Rh ₂ (S-TBSP) ₄ (161b , Chart 4), hexane, reflux, 1 h Rh ₂ (R-TBSP) ₄ (<i>ent</i> - 161b , Chart 4), I (99) de = 53% hexane, reflux, 1 h	I (72) de = 79% I (97) de = 80% I (99) de = 53%	177 177 177	
C ₁₀ R =					
		Rh ₂ (OOct) ₄ , hexane, reflux, 1 h Rh ₂ (S-TBSP) ₄ (161b , Chart 4), hexane, reflux, 1 h Rh ₂ (R-TBSP) ₄ (<i>ent</i> - 161b , Chart 4) hexane, reflux, 1 h	I (82) dc = 94% I (83) de = 20% I (67) de = 70%	177 177 177	
		Rh ₂ (OOct) ₄ , hexane, reflux, 1 h			
C ₁₀ -C ₁₃			de (%) abs stereochem		
	R ¹	R ²	R ³	R ⁴	
	ethyl (S)-lactate	Me	H	H	(62) 90 1S
	(R)-pantolactone	Me	H	H	(75) 95 1R
	ethyl (S)-lactate	H	Me	H	(81) 75 1S
	(R)-pantolactone	H	Me	H	(91) 83 1R
	ethyl (S)-lactate	Me	Me	H	(91) 84 1S
	(R)-pantolactone	Me	Me	H	(69) 94 1R
	ethyl (S)-lactate	H	COMe	H	(74) 79 1S
	(R)-pantolactone	H	COMe	H	(65) 94 1R
	ethyl (S)-lactate	Me	COMe	H	(71) 80 1S
	(R)-pantolactone	H	Me	CO ₂ Me	(65) 82 1R
C ₅			 +		
		Rh ₂ (OAc) ₄ , neat Rh ₂ (OAc) ₄ , neat, rt, 18 h	(-) I:II = 8:1 (60) I:II = 8:1	172 173	

TABLE IX. REACTION OF CARBENOIDS WITH FURANS (Continued)


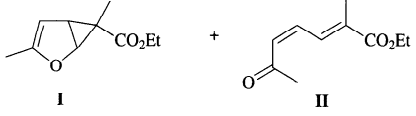
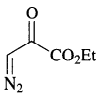

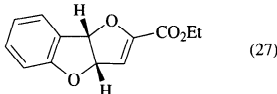
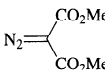

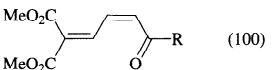
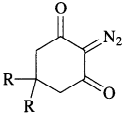
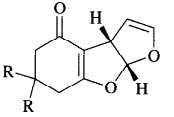

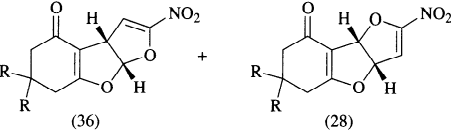

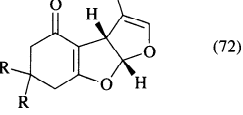

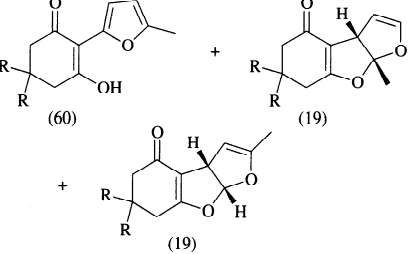

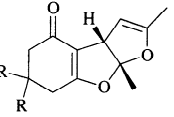

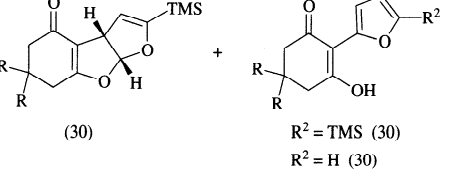
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
				
		Rh ₂ (OAc) ₄ , neat	(-) I:II = 3:1	172
		Rh ₂ (OAc) ₄ , neat, rt, 18 h	(69) I:II = 3:1	173
		Cu-bronze, neat, 110°, 5 h	 (27)	130
		Rh ₂ (OAc) ₄ , neat, rt	 (100)	579
	R = H, Me, CH=CMc ₂			
C₆				
	R		ee (%)	
	H	Rh ₂ (OAc) ₄ , C ₆ H ₅ F, rt, 15 h	(92) —	67
	H	Rh ₂ (OAc) ₄ , neat, rt, 24 h	(48) —	580
	H	Rh ₂ (BNP) ₄ , neat, rt	(44) 50	176
C₈	Me	Rh ₂ (OAc) ₄ , C ₆ H ₅ F, rt, 15 h	(56) —	67
	Me	Rh ₂ (OPiv) ₄ , C ₆ H ₅ F, rt, 15 h	(44) —	67
	Me	Rh ₂ (OAc) ₄ , neat, rt, 24 h	(56) —	580
	Me	Rh ₂ (BNP) ₄ , neat, rt	(50) 49	176
C₆	R = H		Rh ₂ (OAc) ₄ , C ₆ H ₅ F, rt, 15 h	 (36) (28) 67
	R = H		Rh ₂ (OAc) ₄ , C ₆ H ₅ F, rt, 15 h	 (72) 67
	R = H		Rh ₂ (OAc) ₄ , neat, rt, 24 h	 (60) (19) 67, 580
	R = H		Rh ₂ (OAc) ₄ , neat, rt, 24 h	 (36) 67, 580
	R = H		Rh ₂ (OAc) ₄ , C ₆ H ₅ F, rt, 15 h	 (30) R ² = TMS (30) R ² = H (30) 67

TABLE IX. REACTION OF CARBENOIDS WITH FURANS (Continued)


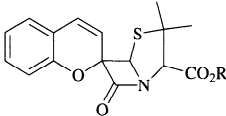

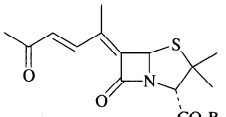

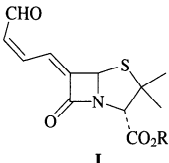
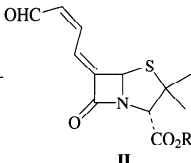
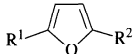
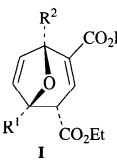
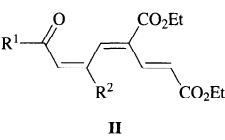
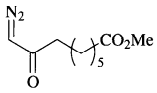
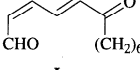
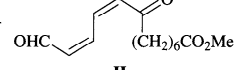
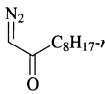
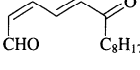
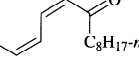
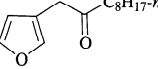
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = POM		Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 1 h	 (15)	161
C ₁₅	R = PNB 	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , 0°, 2 h	 (2.5)	161
C ₂₁	R = CHPh ₂ 	Rh ₂ (OAc) ₄ , neat, 0°, 1 h	 I +  II (100) I:II = 2:1	161
C ₉	 R ¹ R ²	Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , reflux, 20 min	 I +  II	
	R ¹ R ²		R ¹ R ² I II	
	H H		H H (62) (26)	166
	Me H		Me H (45) (14)	167
	Me H		Me H (8) (74)	166
	OMe H		OMe H (28) (44)	167
	Me Me		Me Me (0) (92)	166
	Me TMS		Me (TMS) TMS (Me) (70) (0)	166
	CH ₂ OCH ₃ Me		CH ₂ OCH ₃ (Me) Me (CH ₂ OCH ₃) (80) (0)	167
			CH ₂ OCH ₃ (Me) Me (CH ₂ OCH ₃) (61) (0)	166
			CH ₂ OCH ₃ (Me) Me (CH ₂ OCH ₃) (54) (0)	166
C ₁₀		Rh ₂ (OAc) ₄	 I +  II (-) I:II = 5:1	172
		Rh ₂ (OAc) ₄ Rh ₂ (OAc) ₄ , neat, rt, 18 h	 I +  II +  III (-) I:II:III = 7:1:1 (79) I:II:III = 7:1:1	172 173

TABLE IX. REACTION OF CARBENOIDS WITH FURANS (Continued)

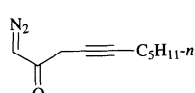

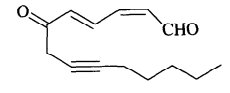
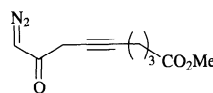

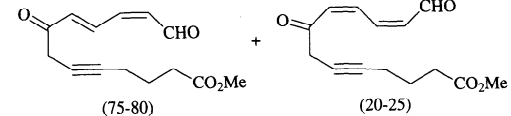
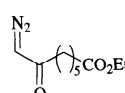
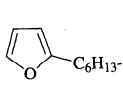
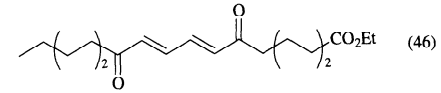
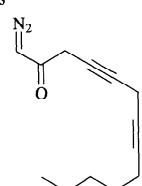

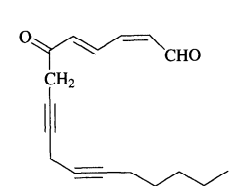
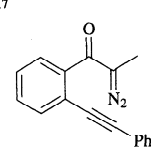

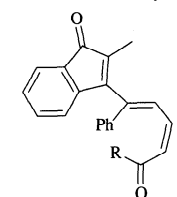
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Rh ₂ (OAc) ₄ , neat, rt, 1 h	 (—)	169
		Rh ₂ (OAc) ₄ , neat, rt, 2 h	 (75-80) + (20-25)	164, 168
		1. Rh ₂ (OAc) ₄ , CH ₂ Cl ₂ , rt, 12 h 2. I ₂ , CH ₂ Cl ₂ , rt, 2 h	 (46)	170
C₁₃ 		Rh ₂ (OAc) ₄	 (—)	164, 168
C₁₇ 		Rh ₂ (OAc) ₄ , neat, rt, 30 min	 (91) (94)	581
	R H Me			

TABLE X. REACTION OF CARBENOIDS WITH PYRROLES


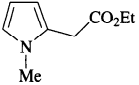
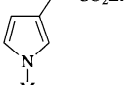
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																														
C ₂ N ₂ =CH-CO ₂ R			 + 																																																																															
C ₄ R = Et			<table border="1"> <thead> <tr> <th></th> <th>I+II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Cu powder, 110°</td> <td>(31)</td> <td>81:19</td> </tr> <tr> <td>Cu-bronze, 100°</td> <td>(30-40)</td> <td>84-79:21-16</td> </tr> <tr> <td>Cu₂O, 100°</td> <td>(45)</td> <td>80:20</td> </tr> <tr> <td>CuSO₄, 80°</td> <td>(58)</td> <td>65:35</td> </tr> <tr> <td>Cu(OAc)₂, 80°</td> <td>(45)</td> <td>81:19</td> </tr> <tr> <td>Cu(NO₃)₂, 55°</td> <td>(54)</td> <td>71:29</td> </tr> <tr> <td>CuCN, 70°</td> <td>(43)</td> <td>76:24</td> </tr> <tr> <td>Cu(BF₄)₂, 50°</td> <td>(66)</td> <td>54:46</td> </tr> <tr> <td>Cu(OSO₂CF₃)₂, 40°</td> <td>(63)</td> <td>58:42</td> </tr> <tr> <td>CuCl, 75°</td> <td>(48)</td> <td>80:20</td> </tr> <tr> <td>CuCl·P(OEt)₃, 60°</td> <td>(51)</td> <td>81:19</td> </tr> <tr> <td>CuBr, 60°</td> <td>(27)</td> <td>80:20</td> </tr> <tr> <td>CuBr·P(OEt)₃, 65°</td> <td>(34)</td> <td>82:18</td> </tr> <tr> <td>CuI, 75°</td> <td>(34)</td> <td>81:19</td> </tr> <tr> <td>CuI·(POEt)₃, 65°</td> <td>(27)</td> <td>84:16</td> </tr> <tr> <td>CuF₂, 80°</td> <td>(43)</td> <td>85:15</td> </tr> <tr> <td>CuCl₂, 75°</td> <td>(42)</td> <td>82:18</td> </tr> <tr> <td>CuBr₂, 60°</td> <td>(33)</td> <td>81:19</td> </tr> <tr> <td>Cu(OMe)₂, 60°</td> <td>(45)</td> <td>83:17</td> </tr> <tr> <td>Pd(OAc)₂, 30°</td> <td>(35)</td> <td>66:34</td> </tr> <tr> <td>(π-C₃H₅PdCl)₂, 35°</td> <td>(42)</td> <td>67:33</td> </tr> <tr> <td>DiphosNiCl₂, 90°</td> <td>(13)</td> <td>67:33</td> </tr> <tr> <td>ZnI₂, 110°</td> <td>(~3)</td> <td>—</td> </tr> <tr> <td>LiClO₄, 110°</td> <td>(15)</td> <td>—</td> </tr> <tr> <td>Rh₂(OAc)₄, 80°</td> <td>(trace)</td> <td>—</td> </tr> </tbody> </table>		I+II	I:II	Cu powder, 110°	(31)	81:19	Cu-bronze, 100°	(30-40)	84-79:21-16	Cu ₂ O, 100°	(45)	80:20	CuSO ₄ , 80°	(58)	65:35	Cu(OAc) ₂ , 80°	(45)	81:19	Cu(NO ₃) ₂ , 55°	(54)	71:29	CuCN, 70°	(43)	76:24	Cu(BF ₄) ₂ , 50°	(66)	54:46	Cu(OSO ₂ CF ₃) ₂ , 40°	(63)	58:42	CuCl, 75°	(48)	80:20	CuCl·P(OEt) ₃ , 60°	(51)	81:19	CuBr, 60°	(27)	80:20	CuBr·P(OEt) ₃ , 65°	(34)	82:18	CuI, 75°	(34)	81:19	CuI·(POEt) ₃ , 65°	(27)	84:16	CuF ₂ , 80°	(43)	85:15	CuCl ₂ , 75°	(42)	82:18	CuBr ₂ , 60°	(33)	81:19	Cu(OMe) ₂ , 60°	(45)	83:17	Pd(OAc) ₂ , 30°	(35)	66:34	(π-C ₃ H ₅ PdCl) ₂ , 35°	(42)	67:33	DiphosNiCl ₂ , 90°	(13)	67:33	ZnI ₂ , 110°	(~3)	—	LiClO ₄ , 110°	(15)	—	Rh ₂ (OAc) ₄ , 80°	(trace)	—	
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TABLE X. REACTION OF CARBENOIDS WITH PYRROLES (Continued)


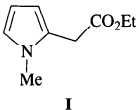
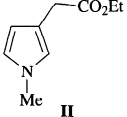
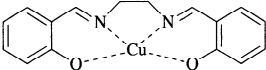

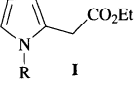
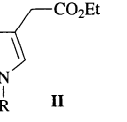

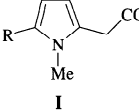
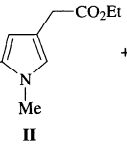
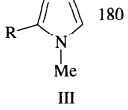
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																												
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			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I+II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>(34-42)</td> <td>91-93:9-7</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>(44-45)</td> <td>90-91:10-9</td> </tr> <tr> <td>Me</td> <td>CF₃</td> <td>(54)</td> <td>80:20</td> </tr> <tr> <td>CF₃</td> <td>CF₃</td> <td>(55)</td> <td>78-80:22-20</td> </tr> </tbody> </table>	R ¹	R ²	I+II	I:II	Me	Me	(34-42)	91-93:9-7	Me	Ph	(44-45)	90-91:10-9	Me	CF ₃	(54)	80:20	CF ₃	CF ₃	(55)	78-80:22-20																									
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CF ₃	CF ₃	(55)	78-80:22-20																																													
$\left[\begin{array}{c} \text{R}^1 \\ \\ \text{C}_6\text{H}_3\text{O} \\ \\ \text{X} \end{array} \right]_2 \text{Cu}^{2+}$	180																																															
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TABLE X. REACTION OF CARBENOIDS WITH PYRROLES (Continued)

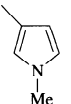
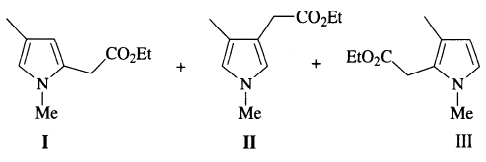
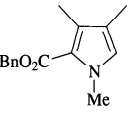
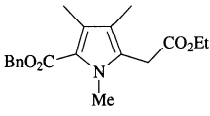
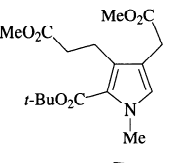
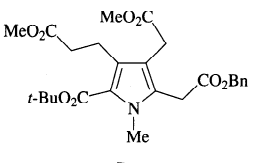
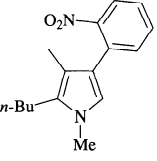
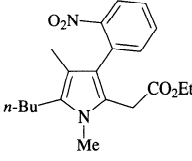
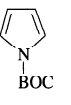
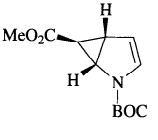
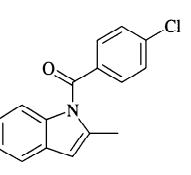
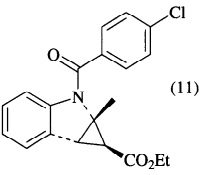
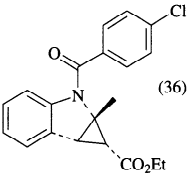
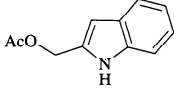
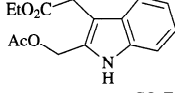
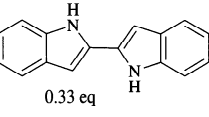
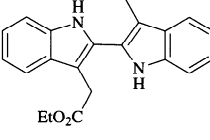
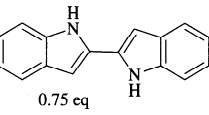
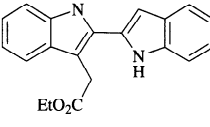
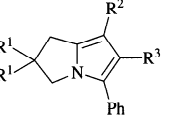
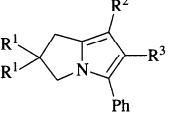
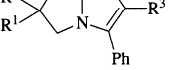
Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																									
R = Et			 I + II + III	180																									
			<u>I:II:III</u> (65) 57:14:29 (74) 40:30:30																										
R = Et		Cu-bronze	 (43)	66																									
R = Bn		Cu powder, 90°	 (25)	582																									
R = Et		Rh ₂ (OAc) ₄	 (27)	583																									
C ₃ R = Me		Rh ₂ (OAc) ₄	 (45)	183																									
R = Et		Cu-bronze	 (11) +  (36)	584																									
C ₄ R = Et		Cu-bronze	 (55)	584																									
R = Et	 0.33 eq	Cu powder	 (41)	585																									
R = Et	 0.75 eq	Cu powder	 (16)	585																									
R = Et		Cu powder	 I: R ² = Ph, R ³ = CH ₂ CO ₂ Et  II: R ² = CH ₂ CO ₂ Et, R ³ = Ph	217																									
	<table border="1" data-bbox="581 1951 729 2089"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Ph</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>Ph</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Ph</td> </tr> </tbody> </table>	R ¹	R ²	R ³	H	Ph	H	H	H	Ph	Me	Ph	H	Me	H	Ph		<table border="1" data-bbox="1032 1951 1154 2089"> <thead> <tr> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>(16)</td> <td>(0)</td> </tr> <tr> <td>(0)</td> <td>(25)</td> </tr> <tr> <td>(19)</td> <td>(0)</td> </tr> <tr> <td>(0)</td> <td>(31)</td> </tr> </tbody> </table>	I	II	(16)	(0)	(0)	(25)	(19)	(0)	(0)	(31)	
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TABLE X. REACTION OF CARBENOIDS WITH PYRROLES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Me		Rh ₂ (S-TBSP) ₄ (161b), hexane	 ee (%) (42) 51 (44) 42 (46) 17 (34) 29	175
R = Me C ₈ R = CH ₂ CO ₂ Et		Rh ₂ (S-TBSP) ₄ (161b), hexane	 (42) (62) ee = 51% + (12) (13)	175, 586 586
			 I + II + III + IV	
C ₅ R = Me		Rh ₂ (S-TBSP) ₄ (161b), hexane	I (24) II (6) III (19) IV (21)	175
		Rh ₂ (OOct) ₄ , hexane	(38) (16) (10) (27)	586
C ₈ R = CH ₂ CO ₂ Et		Rh ₂ (OOct) ₄ , hexane	(56) (8) (8) (12)	586
C ₅ R = Me C ₆ R = Et		Rh ₂ (OOct) ₄ , hexane	 (56) (33)	587
C ₅ R = Me		Rh ₂ (OOct) ₄ , hexane	 (73) + (-)	185
C ₁₂ Et C ₁₁ Me C ₁₄ Et		Rh ₂ (OAc) ₄	 (61) (53) (18)	184
	R ¹ R ² Et SO ₂ Ph Me Ph Et CH=CHPh			

TABLE X. REACTION OF CARBENOIDS WITH PYRROLES (Continued)

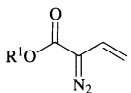
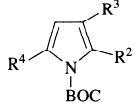
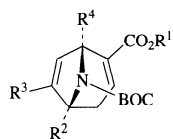
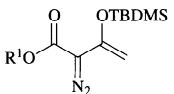
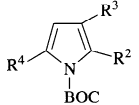
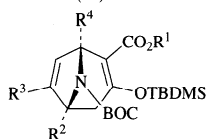
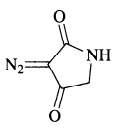
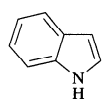
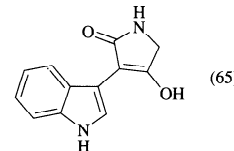
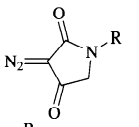
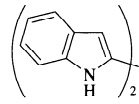
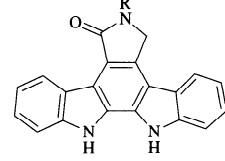
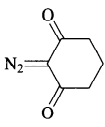
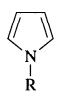
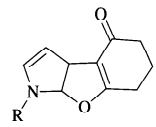

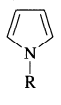
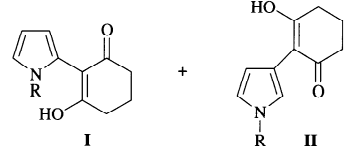
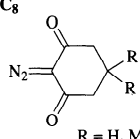
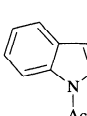
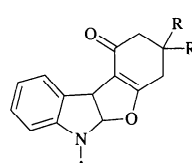
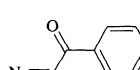

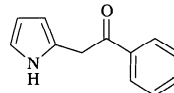
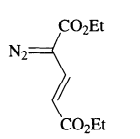

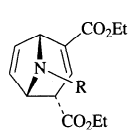
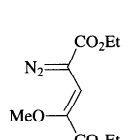

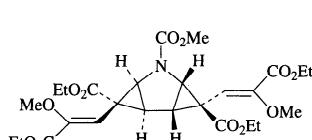
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TABLE X. REACTION OF CARBENOIDS WITH PYRROLES (Continued)

Carbenoid Precursor	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₆-C₈</p>  <p>R = H, Me</p>		Rh ₂ (OAc) ₄ , C ₆ H ₅ F	 <p>R H (54) Me (54)</p>	580, 67
<p>C₈</p> 		Cu powder	 <p>(32)</p>	589
<p>C₉</p> 	 <p>R CO₂Me CO₂Et CO₂CH₂CH₂TMS</p>	Rh ₂ (OAc) ₄	 <p>(62) (54) (71)</p>	184
<p>C₁₀</p> 		Rh ₂ (OAc) ₄	 <p>(33)</p>	184

10. Acknowledgments

We are indebted to our colleagues in the Davies Group (Dr. Rebecca Calvo, Jason De Meese, Dr. Monica Grazini, Dr. Timothy Gregg, Dr. Tore Hansen, Dr. L. Mark Hodges, Melinda Hodges, Dr. Darrin Hopper, Michael Levitt, Dr. Tadamichi Nagashima, Stephen Panaro, Dr. Pingda Ren, Leatte Rusiniak, Douglas Stafford, Dr. Robert Townsend, Chandrasekar Venkataramani, and Yasuno Yokota) at the State University of New York at Buffalo for their assistance in assembling the references, and their assistance in reviewing the manuscript. We also thank Angela Davies and Diane Witczak for their assistance in assembling the references and their patience with us through the preparation of this manuscript, as well as Catherine Antoulinakis for her assistance in organizing the references and record keeping. We gratefully acknowledge the guidance and assistance of the editorial staff of *Organic Reactions*, in particular Dr. Linda Press and Professor Amos B. Smith III, during the preparation of this chapter.

Warning: Great care should be taken in handling diazo compounds because they are potentially toxic and can have explosive properties. Therefore, diazo compounds should be handled carefully and all reactions should be carried out in a well-vented fume hood behind a blast shield.

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Abbreviations

abs: absolute

p-ABSA: *p*-acetamidobenzenesulfonyl azide

Ac: acetyl

acac: acetylacetonate

aq: aqueous

BHT: 2,6-bis-*tert*-butyl-4-methylphenolyl

Bn: benzyl

BOC: *tert*-butoxycarbonyl

BNP: binaphthyl phosphate

BSI: *N-tert*-butyl salicylimide

Bz: benzoyl

CBZ: benzyloxycarbonyl

COD: cyclooctadiene

Cp: cyclopentadiene

Cy: cyclohexyl

DBU: 1,5-diazabicyclo[5.4.0]undec-5-ene

DCE: 1,2-dichloroethane

DCM: dicyclohexylmethyl

DDQ: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

de: diastereomeric excess

Diphos: 1,2-bis(diphenylphosphino)ethane

DME: 1,2-dimethoxyethane

DMF: *N,N*-dimethylformamide

DPMS: diphenylmethylsilyl

Dppe: 1,2-bis(diphenylphosphino)ethane

EDA: ethyl diazoacetate

ee: enantiomeric excess

ether: diethyl ether

c-hex: cyclohexyl

Hex: Hexane

LDA: lithium diisopropyl amide

LiHMDS: lithium hexamethyldisilylamide

MOM: methoxymethyl

Naph: naphthyl

Oct: octanoate

OEP: octaethylporphyrin

PE: polyethylene

Pfb: perfluorobutyrate

Pip: piperidine

Piv: pivalate

PMB: *p*-methoxybenzyl

PNB: *p*-nitrobenzyl

POM: pivaloyloxymethyl

Pr: propyl

pyr: pyridine

rt: room temperature

sat.: saturated

SC: supercritical

TBAF: tetrabutylammonium fluoride

TBDMS: *tert*-butyldimethylsilyl

TCE: 1,1,2,2-tetrachloroethane

TES: triethylsilyl

Tf: trifluoromethanesulfonyl

TFA: trifluoroacetic acid

THF: tetrahydrofuran

THP: 2-tetrahydropyranyl

TMP: tetramesitylporphyrin

TMS: trimethylsilyl

TPA: triphenyl acetate

TpFPP: tetra(hexafluorophenyl)porphyrin

Ts: *p*-toluenesulfonyl

***p*-TsOH:** *p*-toluenesulfonic acid

TTP: tetra(*p*-tolyl)porphyrin

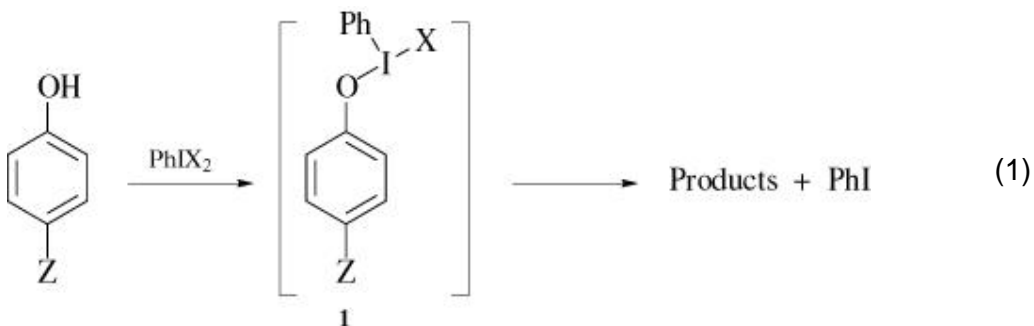
Oxidation of Phenolic Compounds with Organohypervalent Iodine Reagents

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Om Prakash [#], The University of Illinois at Chicago, Chicago, Illinois

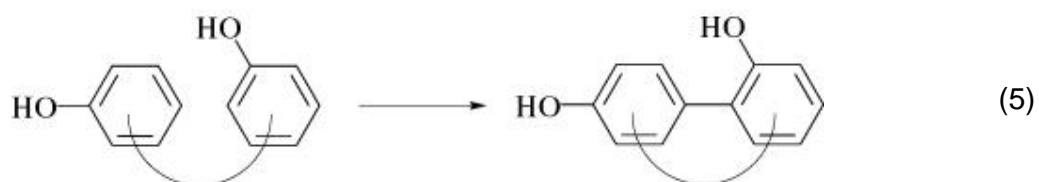
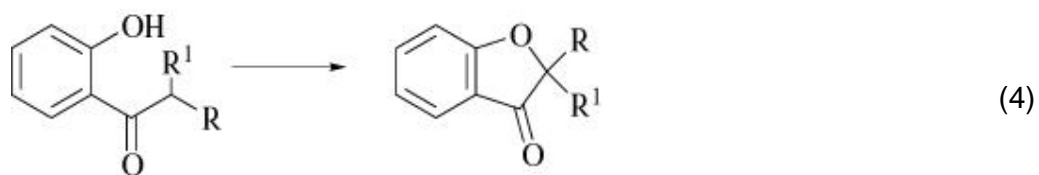
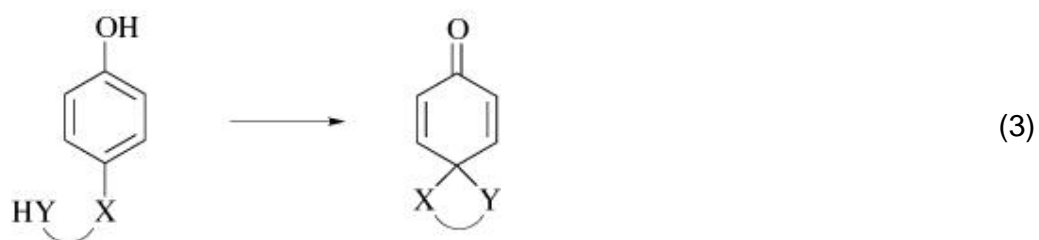
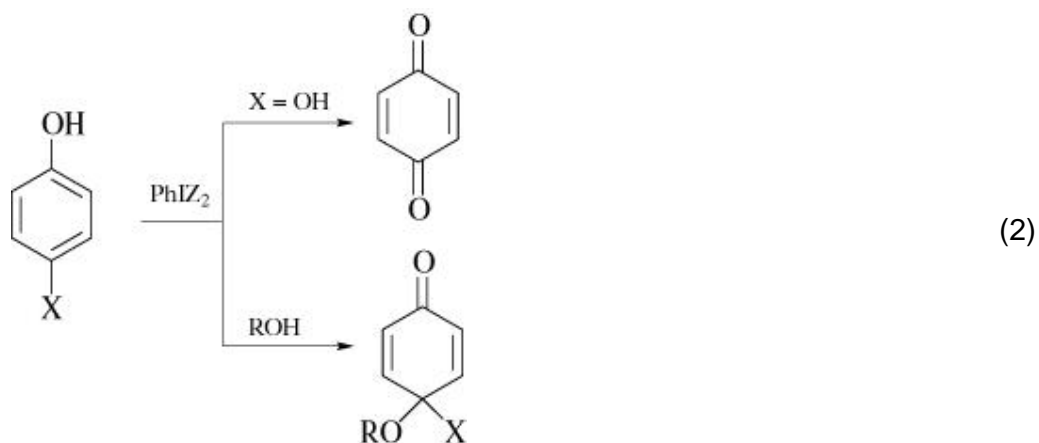
1. Introduction

The oxidation of phenols is a key biochemical process in oxidative phosphorylation, and it is also important in numerous biosynthetic pathways. (1-12) Controlled oxidative transformations of substituted phenols are found in many synthetic organic sequences. Accordingly, a large number of oxidizing agents for phenols have been developed. Useful reagents include Fremy's salt ($(\text{KSO}_3)_2\text{NO}$), (13) and a wide variety of other redox metal-based oxidants such as Pb(IV), (14) Mn(III), (15) Tl(III), (16, 17) Cu(II), (18) and Fe(III). (19-25) Recently, organohypervalent iodine reagents have emerged as particularly useful agents for oxidizing phenols. (26-47a) In the area of natural product synthesis, organohypervalent iodine reagents have been used extensively to effect oxidative intramolecular bicyclization and spirocyclization. The focus of this chapter is on synthetic applications. The chapter also covers formation and applications of phenolic iodonium ylides. (28, 40)

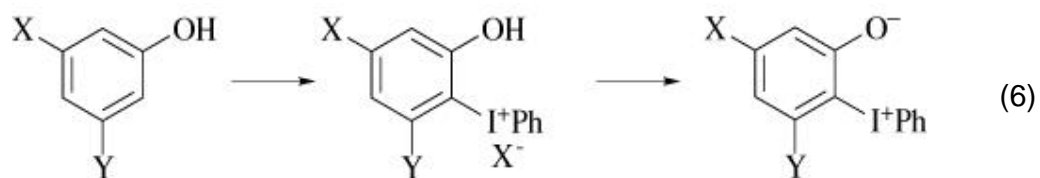
The processes that occur during the oxidation of phenols with organohypervalent iodine reagents can be divided into two categories. The first category involves ligand exchange of the phenolic proton with the hypervalent iodine reagent to generate the O-I(III) intermediate **1**, which is subsequently transformed to various products, depending upon the reaction conditions (Eq. 1).



These transformations include oxidation of phenols to quinones and related compounds (Eq. 2), formation of spirocyclic and oxygen heterocyclic compounds via oxidative intramolecular participation reactions (Eqs. 3 and 4), and intramolecular carbon-carbon bond formation via phenolic oxidative coupling (Eq. 5). All of these reactions are driven by the reduction of iodine(III) [or iodine(V)] to iodine(I) (iodobenzene).

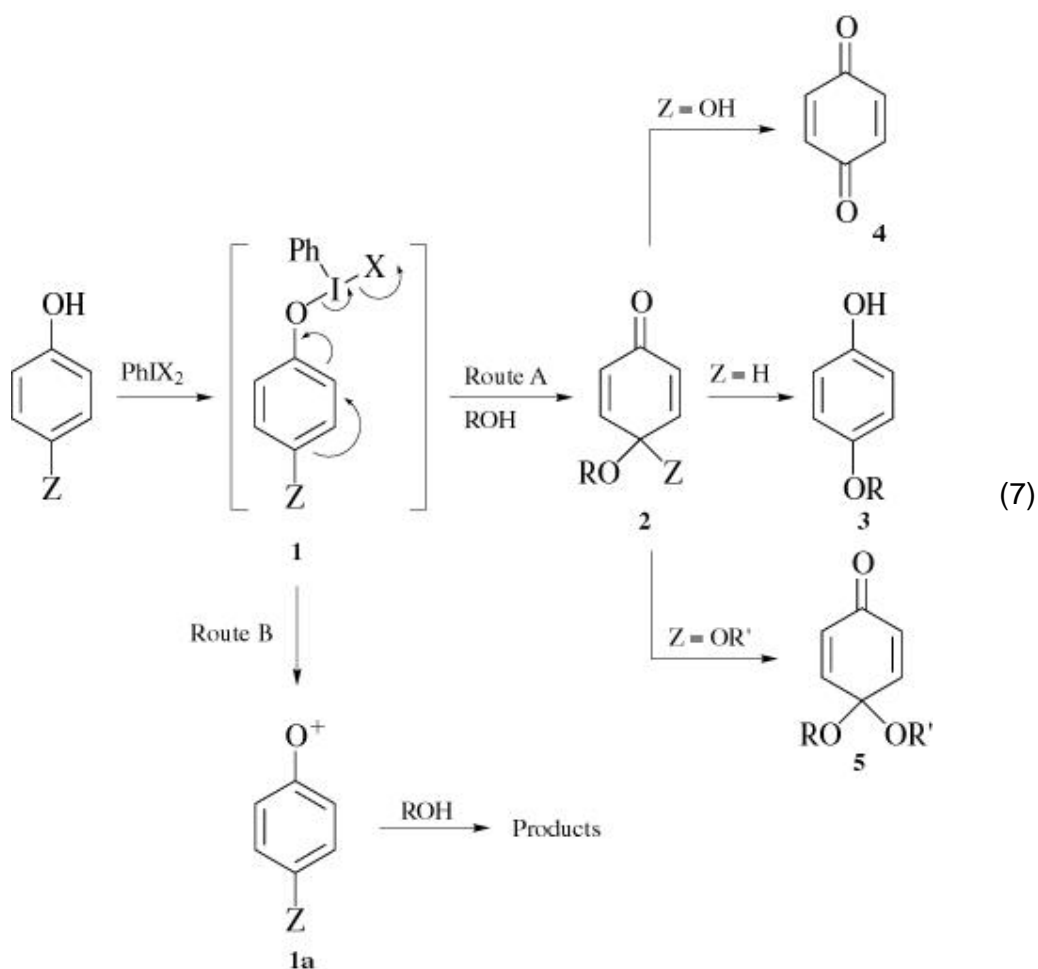


A second class of reactions that is discussed in this chapter includes formation of stable iodonium salts and ylides, which are important intermediates in organic synthesis. These reactions occur via carbon-I(III) bond formation without loss of iodobenzene (Eq. 6).



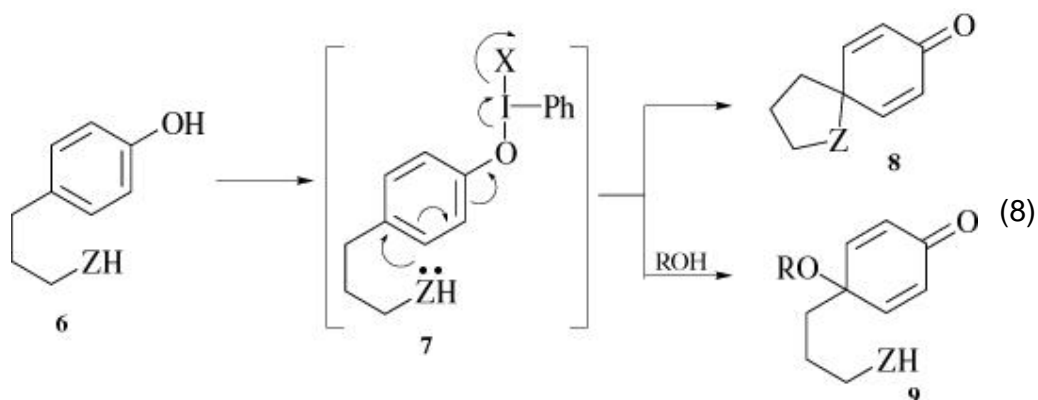
2. Mechanism

Oxidation of phenols provides products that come from a formal two-electron oxidation. These may be formed by a sequential one-electron or two-electron process.



Two pathways (Routes A and B, Eq. 7) have been proposed for the two-electron oxidation of phenols to quinones and related compounds. (48) Common to both pathways is an aryloxyiodonium(III) intermediate **1**, which is formed by ligand exchange between a phenolic hydroxy group and the organohypervalent iodine reagent PhIX_2 . In route A, **1** reacts with nucleophiles such as an alcohol or water to form product **2**. Route B involves dissociation of **1** to the phenoxenium ion **1a**, which then reacts with nucleophiles to give the products.

Product **2** can undergo a proton shift (where $Z^+ = H$) to yield a *para*-substituted phenol (**3**); where Z is hydroxy or alkoxy, a quinone **4** or quinone monoacetal **5** results. Spirobicyclization can be accommodated within this mechanism as resulting from intramolecular participation in the reductive elimination of iodobenzene. In Eq. **8** the group Z attached by a three-atom chain at the *para* position acts as the internal nucleophile.



Thus, either intramolecular spirocyclization (**7**→**8**) or bimolecular attack by a nucleophile or nucleophilic solvent (**7** → **9**) can occur. With an appropriately *meta*-substituted phenol, bicyclization by attack either at the ortho or *para* position is possible.

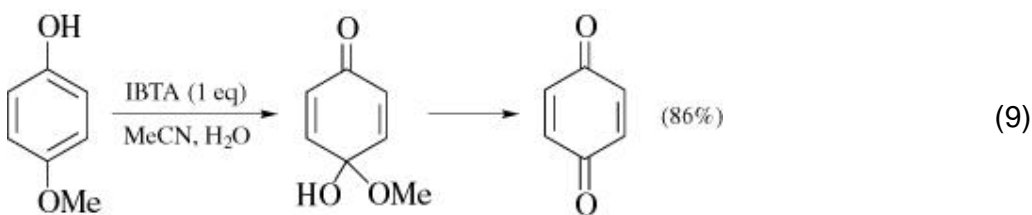
3. Scope and Limitations

3.1. Oxidation of Phenols to Quinones and Related Compounds

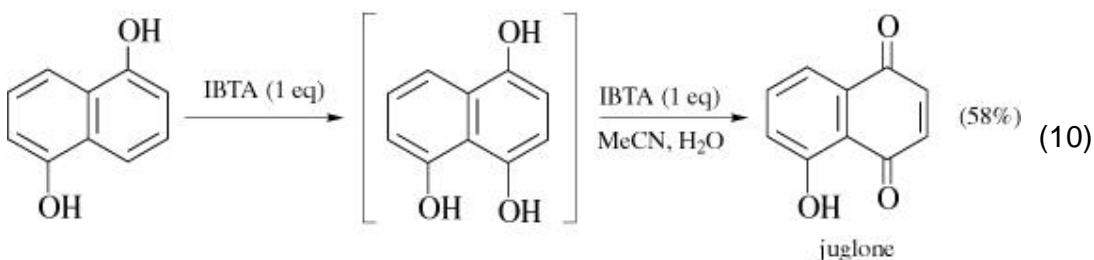
Early studies on the oxidation of phenols with hypervalent iodine reagents reported the formation of resinous products, (48a) and it is only because of recent developments that hypervalent iodine mediated oxidative transformations have become synthetically attractive. Recent work in this area has shown that product distribution among *p*-quinones, *o*-quinones, quinone acetals, and quinone ethers is dependent on: (1) the nature of the phenolic substrates and hypervalent iodine reagents, (2) the nature of the solvent (nucleophilicity and polarity), and (3) the ratio of oxidizing agent to substrate.

3.1.1. Formation of Quinones

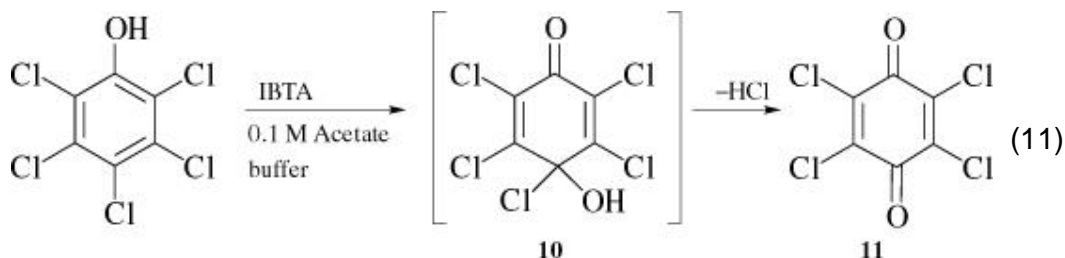
Oxidation of various phenols with organohypervalent iodine reagents under suitable conditions leads to the formation of quinones. Although these transformations have been effected by using various iodine(III) reagents, iodobenzene diacetate [IBD; PhI(OAc)₂] and iodobenzene bis(trifluoroacetate) [IBTA; PhI(O₂CCF₃)₂] are the most efficient. IBD is preferred over IBTA because of its lower toxicity and lower price. The structure of the phenols, the stoichiometry of the reactants, and the reaction conditions affect the course of these oxidations. Phenols containing groups such as alkoxy and *N*-acylamino at the para position are oxidized to *p*-quinones with one equivalent of the I(III), reagent in the presence of water (Eq. 9), (49) whereas phenols without substituents at the para position consume 2 equivalents of oxidant to afford the corresponding



p-quinones (Eq. 10). (50) Water acts as an external nucleophile in these reactions, and hydroquinones are intermediates. (51-53)

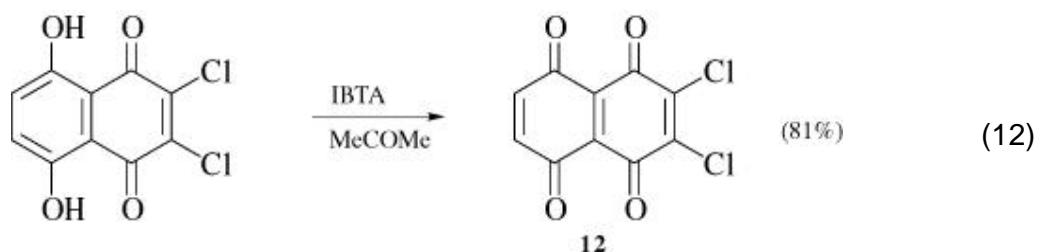


A recent example is the oxidation of pentachlorophenol to tetrachloro-1,4-benzoquinone (**11**) by using IBTA in the presence of acetate buffer (Eq. 11). In this reaction, in situ-generated **10** undergoes loss of one molecule of hydrochloric acid to give **11**. This process offers an analytical method for trace quantities of environmental polychlorophenols. (54)



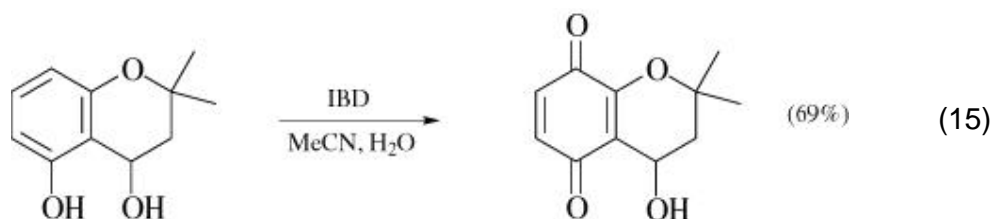
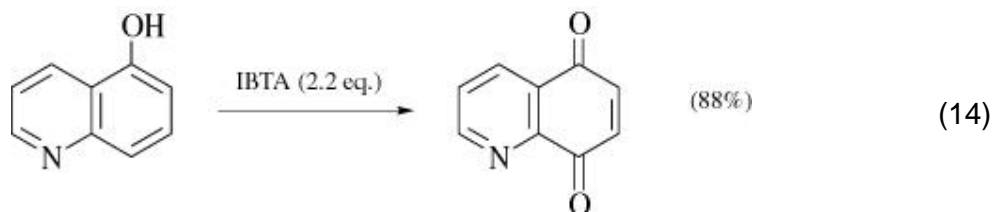
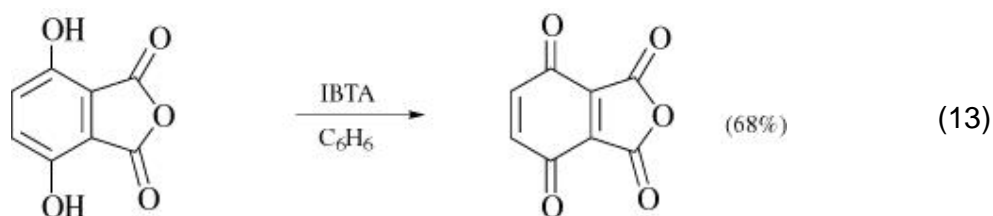
In general, oxidation of phenols yields mixtures of isomeric *p*-benzoquinones and *o*-benzoquinones. However, steric hindrance by the I(III) group such as I(Ph)(O₂CCX₃) can favor formation of *p*-quinones as the major or sole products.

Organohypervalent iodine reagents can also be used for the oxidation of hydrophenols; the reaction requires one equivalent of oxidant. Examples of such oxidations, including additional examples of monophenols, are given in Eqs. 12–15.



Some noteworthy features exemplifying the scope and limitations of this approach are:

1. Quinones such as **12** (Eq. 12), which are useful precursors in the site-selective cycloaddition reactions of bisquinones, are readily accessible through this approach. (55, 56)

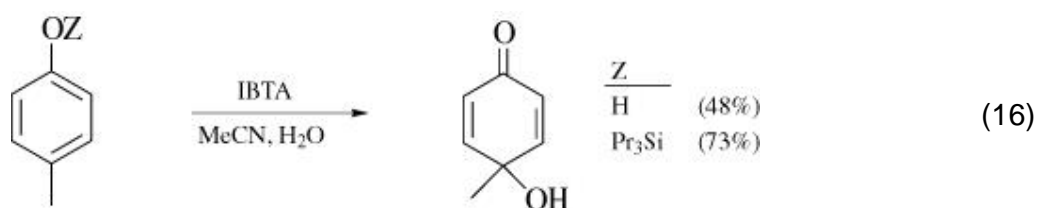


2. The preparation of *p*-benzoquinone-2,3-dicarboxylic acid anhydride using IBTA (Eq. 13) is a notable example, as even fuming nitric acid fails to accomplish this conversion. (57)
3. Phenols containing nitrogen heterocycles are smoothly converted to the corresponding *p*-quinones, leaving the nitrogen unaffected (Eq. 14). (58)
4. The presence of an oxidizable non-phenolic hydroxy group does not interfere with the oxidation process (Eq. 15). (59)
5. An efficient synthesis of 5-hydroxy-1,4-naphthoquinone, juglone (Eq. 10), (50) which is a useful intermediate for the synthesis of tetracyclines (60) and antitumor antibiotics, (61) is available.
6. Phenols containing electron-withdrawing substituents (NO₂, COCH₃, CO₂R) do not give quinones by this method; rather the corresponding iodonium ylides or salts are formed (see Eq. 51).

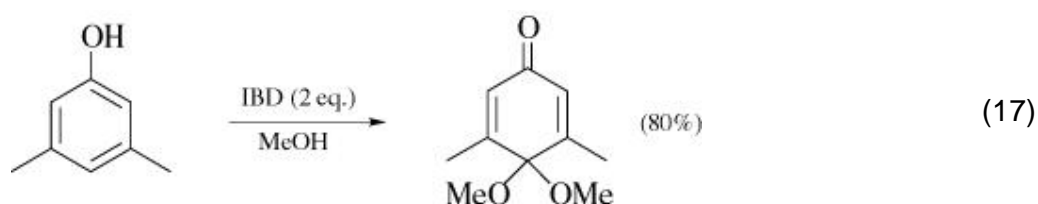
3.2. Formation of *p*-Quinols, *p*-Quinol Ethers, and Quinone Monoacetals

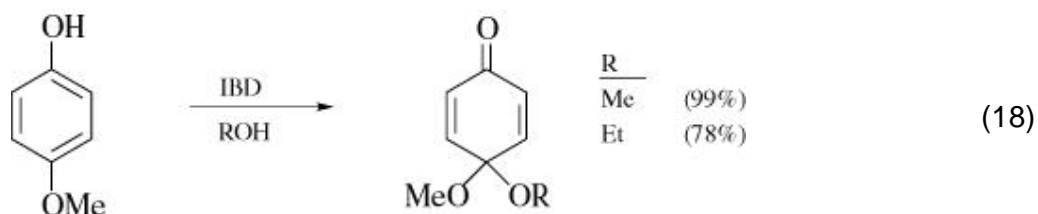
Oxidation of certain *p*-substituted phenols with IBTA in the presence of water affords *p*-quinols. The yields of this reaction can be improved by using the silyl ether derivatives of the phenols. For example, oxidation of the tripropylsilyl ether of *p*-cresol with IBTA in aqueous acetonitrile gives 4-hydroxy-4-methylcyclohexadienone in 73% yield, whereas a 48% yield is obtained from the oxidation of *p*-cresol itself (Eq. 16). (62)

Since phenolic oxidations proceed via an electrophilic intermediate of type 1, the oxidation of phenols has been extensively investigated in the presence of other nucleophiles such as alcohols.



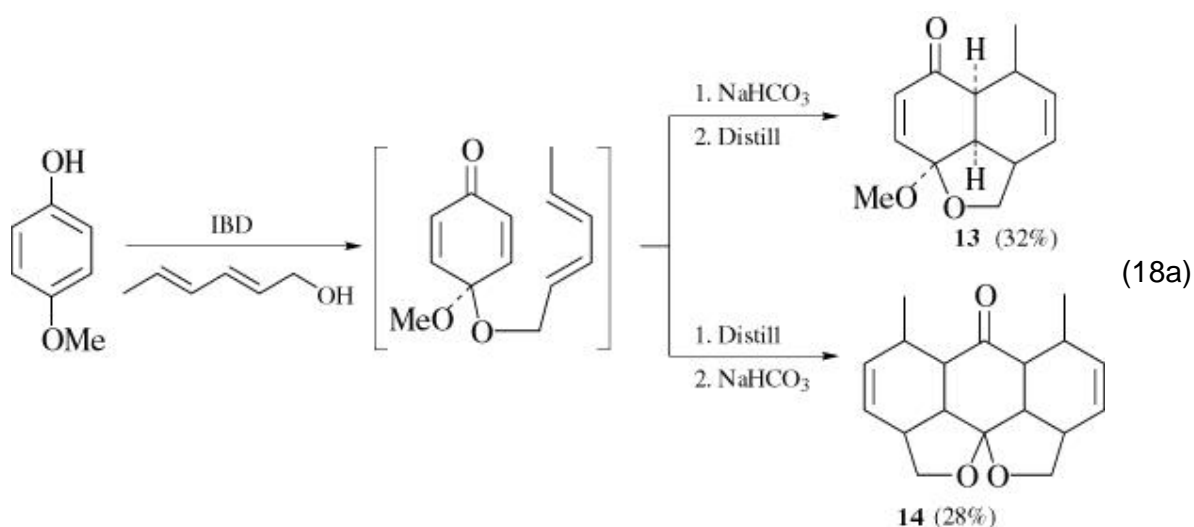
These studies have identified an elegant and general way to synthesize *p*-quinone ethers and 4-bis(alkoxy)cyclohexadienones. Both the stoichiometry and structure of the phenols play a role in determining the course of the reaction. For example, phenols with no substituent at the para position afford quinone monoacetals in good yields upon oxidation with 2 equivalents of IBD in methanol (Eq. 17). (53) On the other hand, oxidation of *p*-alkoxyphenols with one equivalent of the iodine(III) reagent in the presence of methanol or other alcohols results in the formation of corresponding *p*-quinone monoacetals. (53, 63) Thus, oxidation of *p*-methoxyphenol with one equivalent of IBD in methanol or ethanol leads to the formation of quinone monoacetals in high yields (Eq. 18). (53, 63)



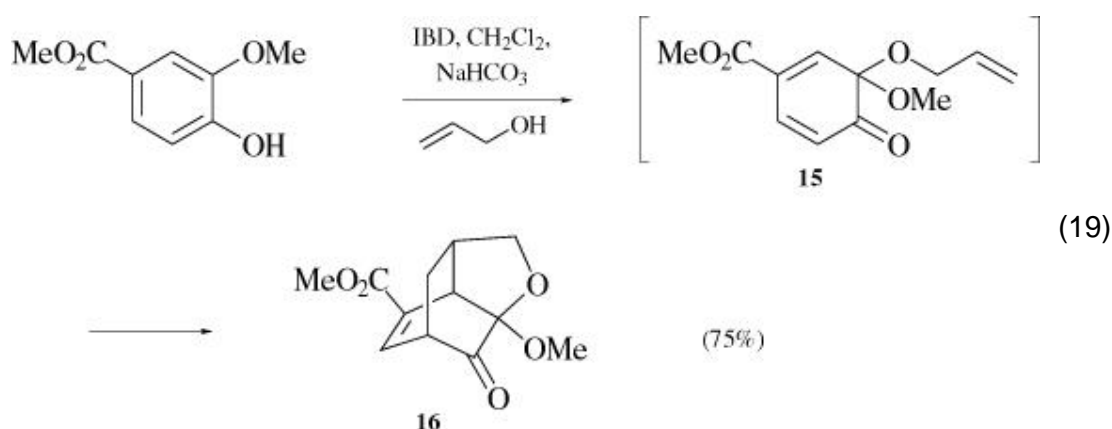


When the alcohol is dienic, nucleophilic addition is followed by an intramolecular Diels-Alder reaction upon the thus-formed *p*-quinone monoacetal. For example, when methanol is replaced by sorbyl alcohol in the above reaction (Eq. 18), in situ intramolecular Diels-Alder reactions proceeding by way of the quinone monoacetal take place. (63) The products from this reaction are found to vary according to the workup employed. Thus, if sodium bicarbonate is added prior to the removal of excess sorbyl alcohol by distillation, **13** is obtained. But if distillation is carried out prior to base addition, the reaction affords only spiroacetal **14**. While the yields of products are modest, these transformations represent a facile, one-pot assembly of a highly functionalized ring system in a single step (Eq. 18a).

Oxidation of phenols bearing an alkoxy substituent at the ortho position results in formation of the corresponding *o*-quinone acetals, which are unstable with respect to dimerization. (63a) *o*-Benzoquinones are generated in situ as dienes in inter- and intramolecular Diels-Alder reactions.

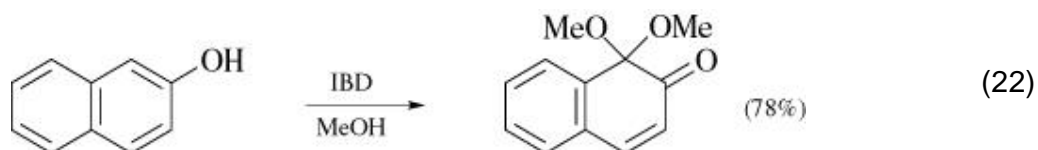
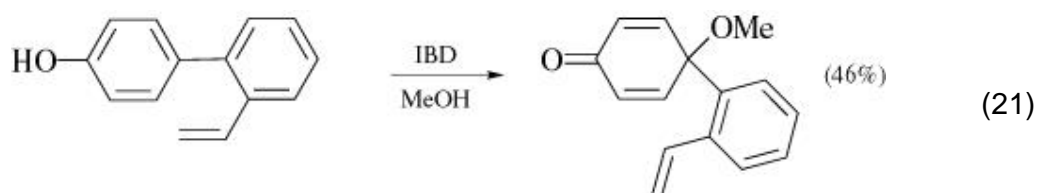
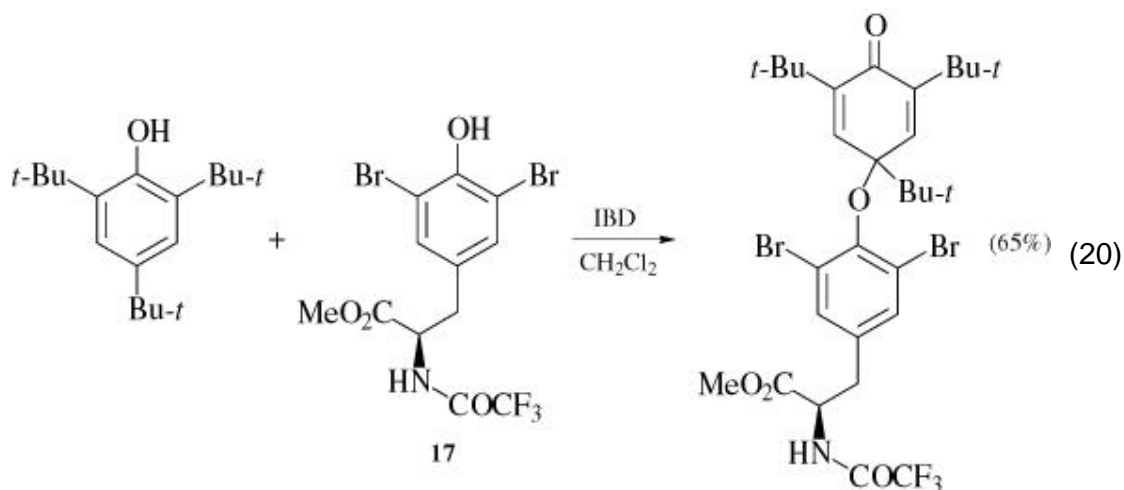


Thus, masked *o*-benzoquinone **15**, generated in situ by the oxidation of methyl vanillate with IBD in dichloromethane containing allyl alcohol, undergoes an intramolecular Diels-Alder reaction to yield **16** (Eq. 19). (64-64a)

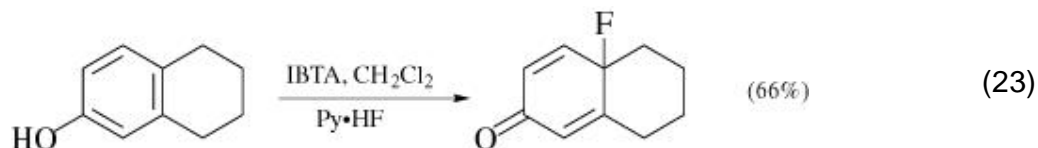


When the para position of the phenol possesses an alkyl or an aryl substituent, *p*-substituted *p*-quinone ethers are the products in these oxidations. A variety of *p*-alkyl/arylphenols, including sterically hindered phenols (Eq. 20), (53, 65) olefinic phenols (Eq. 21), (66) and amidoalkylphenols (67) have been oxidized to quinone monoethers. Eq. 20 illustrates the oxidation of sterically hindered 2,4,6-tri-*tert*-butylphenol in the presence of a phenolic nucleophile 17, and forms the basis of a useful method for the preparation of thyronine derivatives. (68, 69)

Oxidation of α -naphthols with organoiodine(III) reagents affords *p*-naphthoquinone monoacetals, whereas oxidation of β -naphthols leads to stable *o*-naphthoquinone monoacetals (Eq. 22). (70, 71) Both *o*- and *p*-quinone acetals, accessible through I(III) mediated oxidation of phenols, find application in a wide variety of syntheses of hydroxyanthraquinones, benz[*a*]anthraquinones, and related natural products such as anthracyclines. (71-72a)



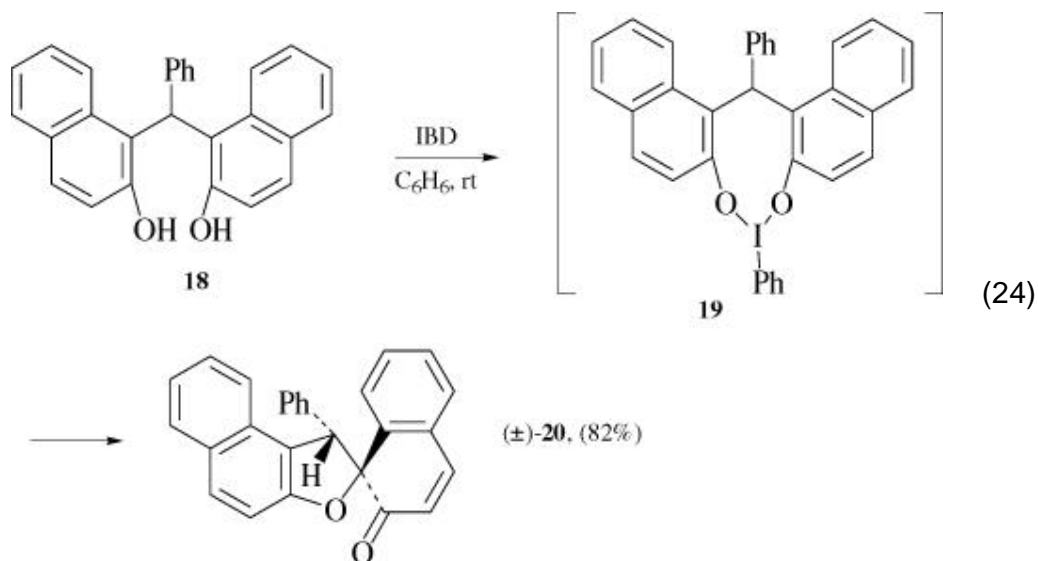
The *ipso* fluorination of *p*-alkylphenols occurs by using IBTA in the presence of pyridinium polyhydrogen fluoride as a source of fluoride anion. The reaction is useful for the synthesis of polycyclic 4-fluorocyclohexa-2,5-dienones (Eq. 23). The presence of alcohols and ketones, which are potentially oxidizable with IBTA, does not interfere in this reaction. (73)



3.3. Intramolecular Participation in the Oxidation of Phenols

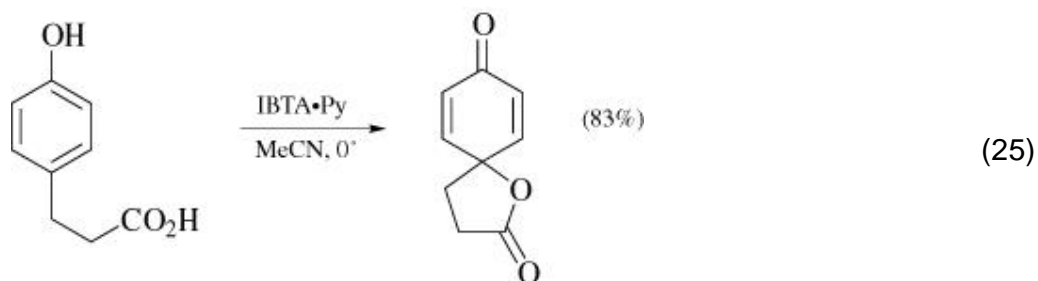
3.3.1. Formation of Heterocyclic Spiroquinones

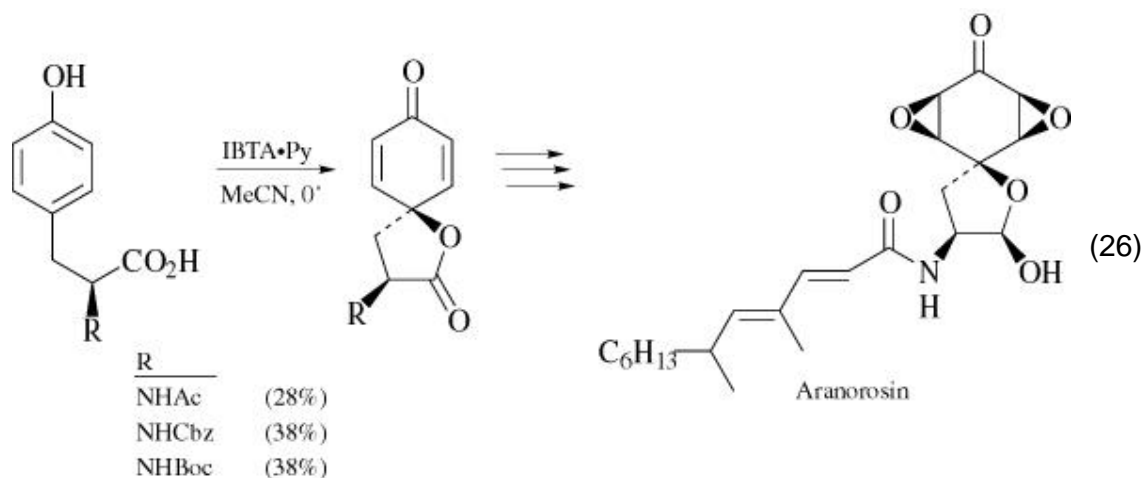
Intramolecular participation leads to spiro compounds when appropriate nucleophilic substituents are present at the ortho or para position of the phenolic compound (Eq. 8). The oxidation of benzylidene-1,1 ϕ -bis(2-naphthols) **18** with IBD in benzene or pyridine results in formation of the less hindered phenylnaphtho[2,1-*b*]furan-2(1*H*)-spiro-1 ϕ (2 ϕ *H*)-naphthalen-2 ϕ -one **20**. This is an example of stereoselective spirocyclization of a phenol where the phenolic hydroxy group acts as the intramolecular nucleophile (Eq. 24). (74, 75)



Although the stereoselectivity of these reactions is attributed to the formation of cyclic intermediate **19**, it is not certain that such an intermediate actually exists, since other bis(naphthols) and related compounds with phenolic hydroxy groups in unfavorable positions undergo similar oxidative spirocyclization.

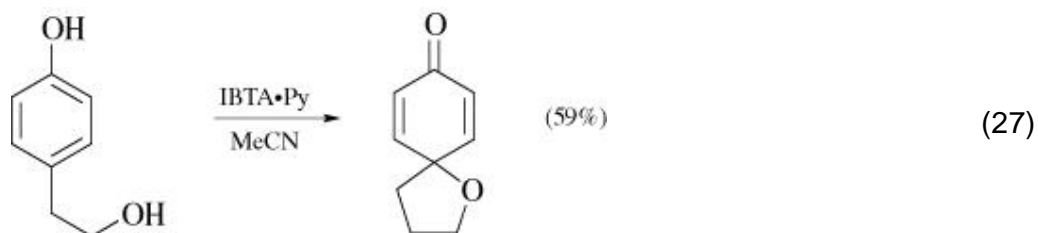
Intramolecular spirocyclization involving the carboxy group as an internal nucleophile occurs when 3-(4-hydroxyphenyl)propanoic acids are oxidized with IBTA or other I(III) reagents (Eq. 25). (76) In most cases non-nucleophilic solvents are required to prevent solvent participation.

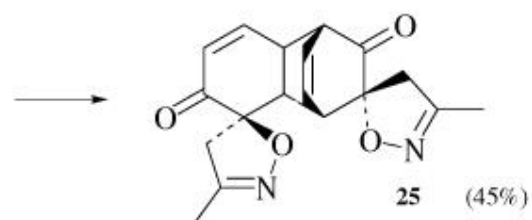
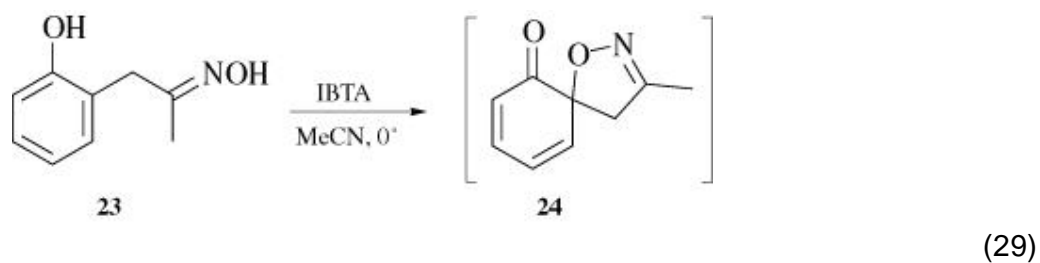
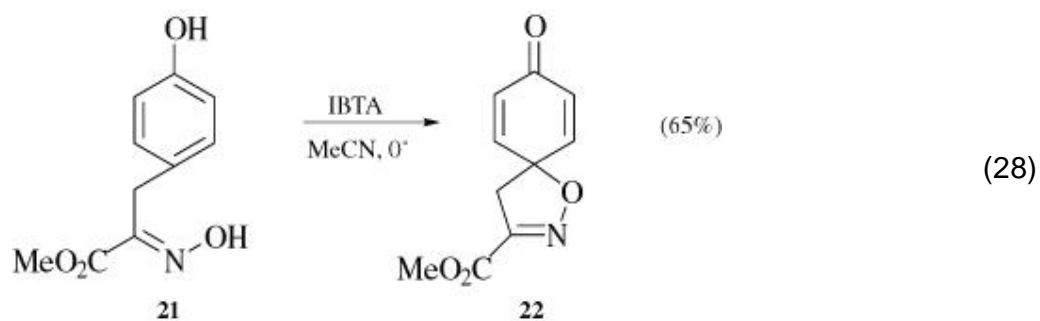




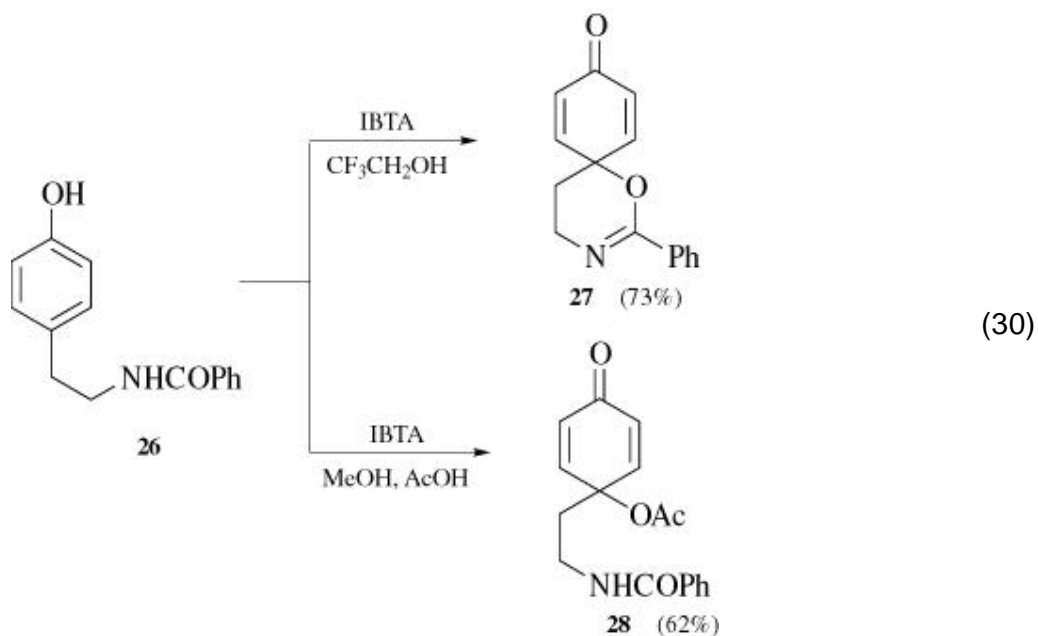
Organoiodine(III)-induced cyclization is applicable to *N*-acyltyrosine derivatives (Eq. 26). (76-78) This approach has been used in the total synthesis of aranorosin, (79, 80) a natural product that is isolated from the fungal strain *Pseudoarachniotus roseus* and is associated with antibiotic, antifungal, and antitumor properties. (81-83)

Oxygen atom participation in the hypervalent iodine oxidation of phenols can also occur with alcoholic groups (Eq. 27 (84-84a)) and oximino groups (Eqs. 28 and 29). While oxidative cyclization of 4-hydroxyphenyl ketoximes **21** smoothly gives the corresponding spirocyclic isoxazolines **22** (Eq. 28), 2-hydroxyphenyl ketoxime **23** produces a Diels-Alder dimer **25** of the expected spirocyclic isoxazoline **24** (Eq. 29). (85) When a chiral *p*-oximino ester is used, asymmetric induction at the para position to the carboalkoxy carbon occurs. (86, 87)

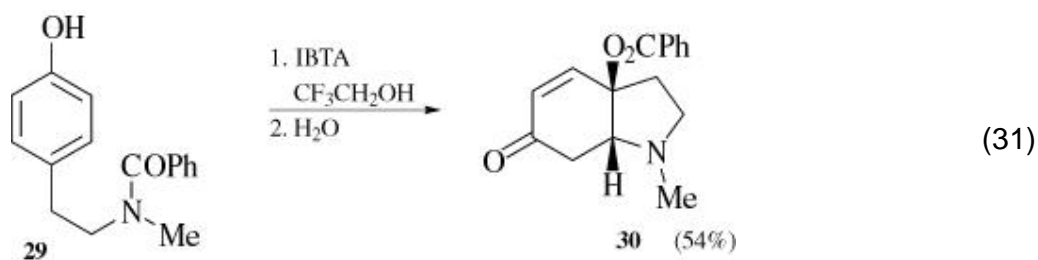




Oxidation of *N*-acyltyramines **26** with IBTA proceeds with intramolecular participation of the amido group oxygen (**26** → **27**) in solvents of low nucleophilicity. In nucleophilic solvents such as methanol and acetic acid, addition of the solvent at the para position occurs (**26** → **28**) (Eq. 30). (67)



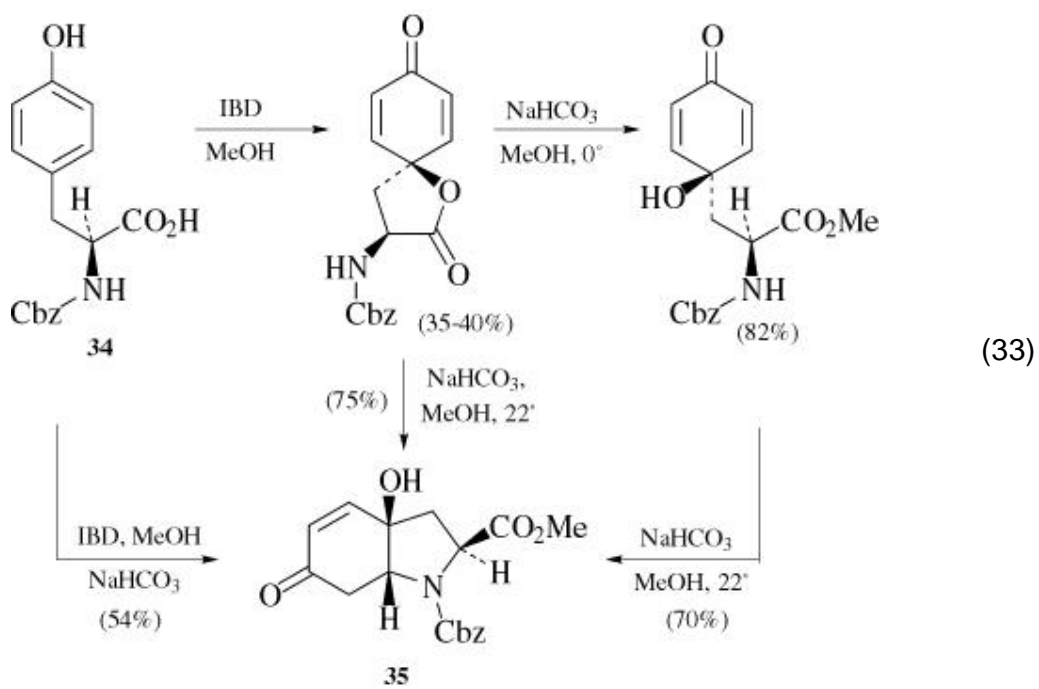
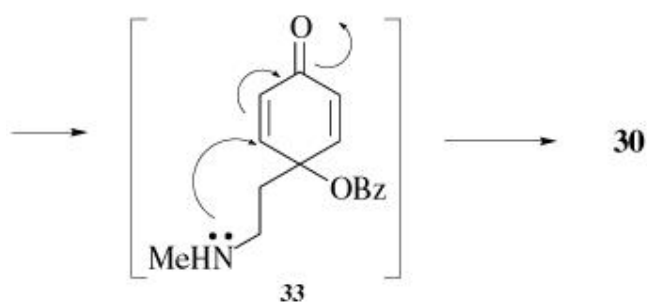
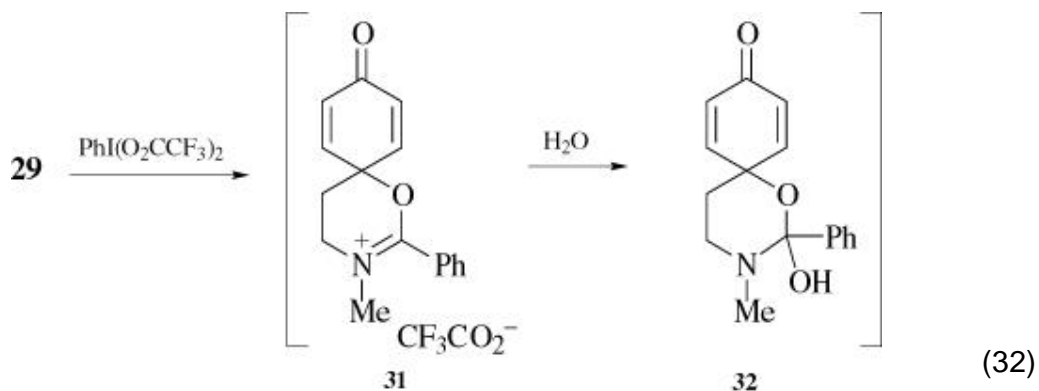
A more complicated example of intramolecular participation in the oxidation of phenols is presented in Eq. 31. In this reaction, oxidation of *N*-methyl-*N*-benzoyltyramine (**29**) with IBTA in the presence of water results in the formation of azabicyclic compound **30**.



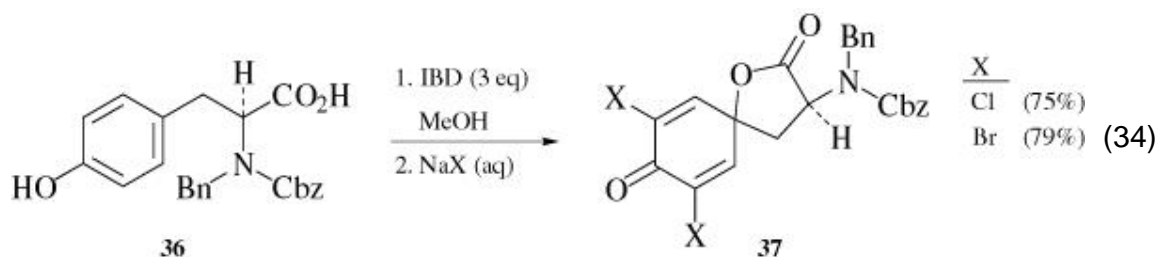
The transformation **29** → **30** is accounted for by intramolecular cyclization to yield the intermediate imidate salt **31**, which is neutralized by water (**31** → **32**) during workup. Ring opening (**32** → **33**) followed by intramolecular Michael addition (**33** → **30**) completes the sequence (Eq. 32).

This strategy of oxidative cyclization followed by intramolecular Michael addition has been used to prepare the core hydrindole ring system **35** of the *Stemona* alkaloids. Oxidation of *N*-protected tyrosine **34** with IBD/ MeOH in the presence of sodium bicarbonate can proceed under three different conditions

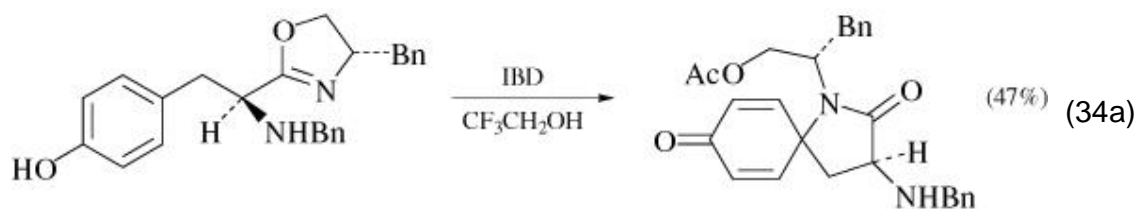
as shown in Eq. 33. These results illustrate an exceptional diastereotopic group-selective intramolecular conjugate addition. (77)



In a related study, it has been observed that oxidation of *N*-benzyl-*N*-benzyloxycarbonyltyrosine (**36**) with 3 equivalents of IBD in acetonitrile followed by quenching with aqueous sodium halide (chloride or bromide) solution gives the corresponding dihalodienone lactone **37** (Eq. 34). (88) With 3-(4-hydroxyphenyl)propanoic acid, oxidation proceeds in the similar manner to afford dihalodienone lactones.



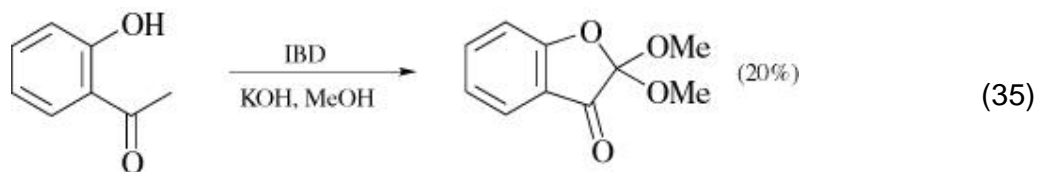
In contrast, oxidation of oxazoline analogs of phenolic compounds with IBD in trifluoroethanol leads to spirocyclic amides (Eq. 34a). (88a) The preferential formation of spirolactones (Eqs. 33, 34) is likely due to an electronic effect.

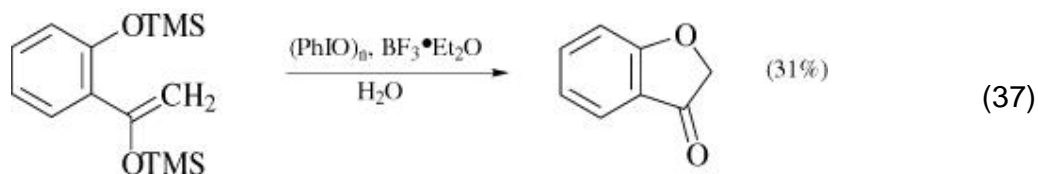
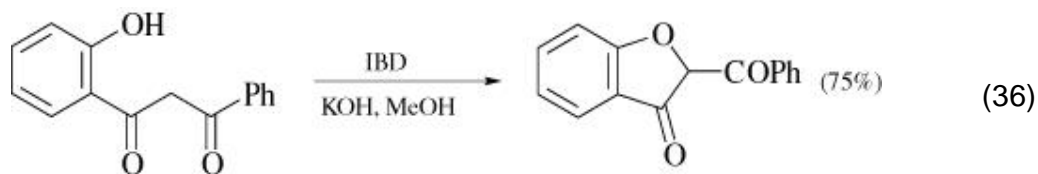


3.4. Formation of Oxygen Heterocyclic Compounds

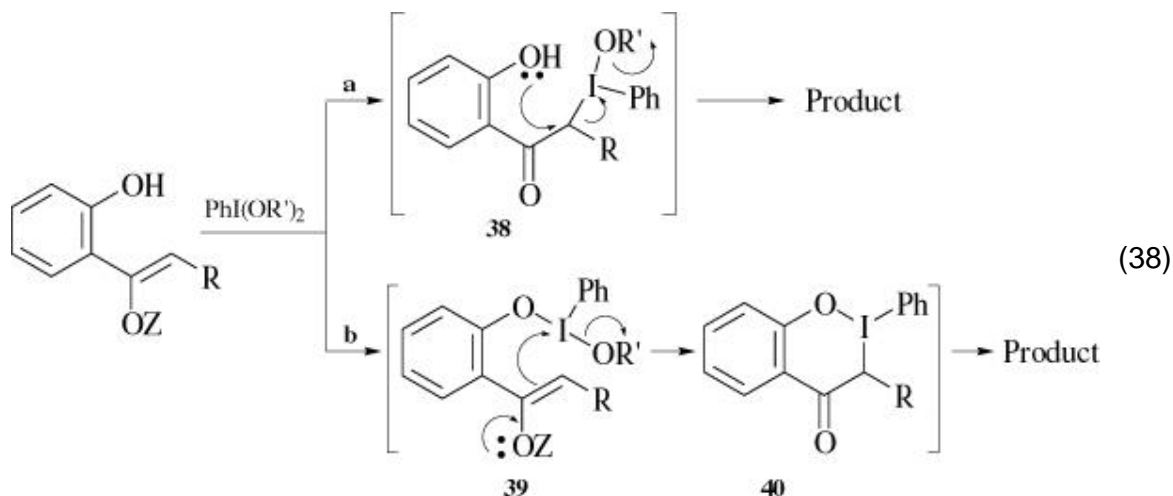
3.4.1. Coumaran-3-ones

Hypervalent iodine oxidation of *o*-hydroxyacetophenones and related compounds under suitable conditions offers convenient syntheses of coumaran-3-ones (Eqs. 35–37). (89-92)



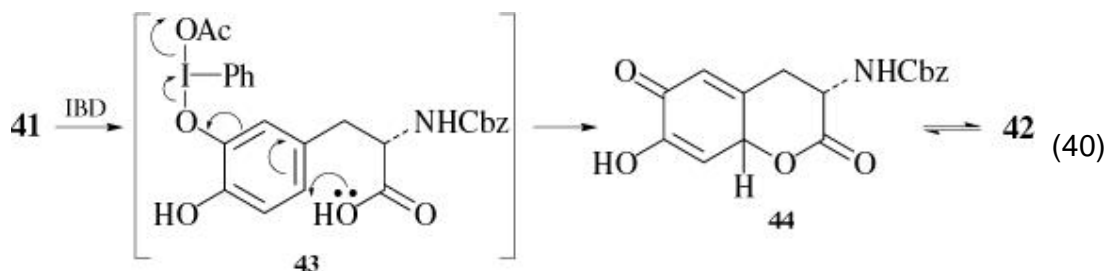
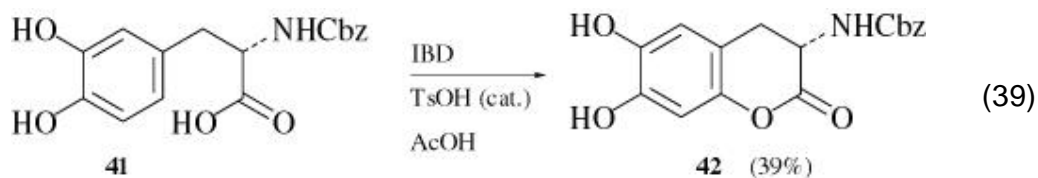


Although these oxidative cyclizations have previously been proposed to occur via intermediates of type **38**, which contain a C-iodine(III) bond (Eq. **38**, route **a**), an alternative route involving oxidation of the phenolic group to form intermediates **39** and **40** also explains these results (Eq. **38**, route **b**).



3.4.2. 3,4-Dihydrocoumarins

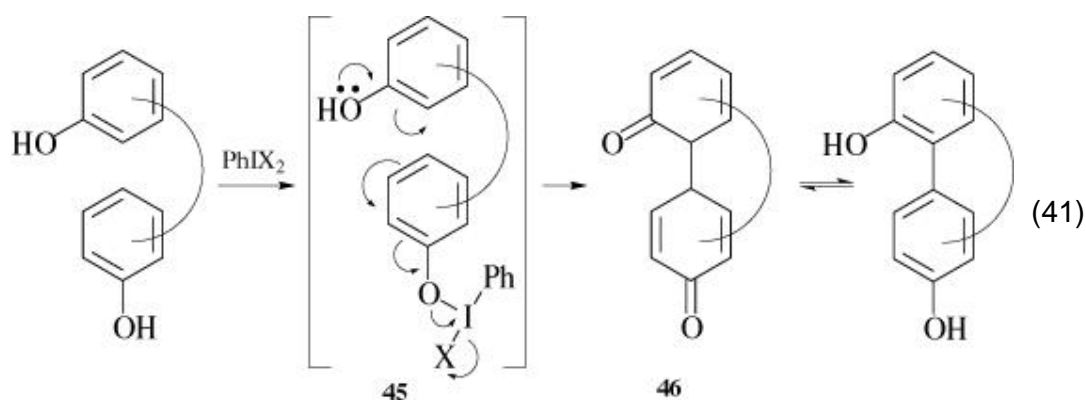
Oxidative cyclization of *N*-acyl-3-(3,4-dihydroxyphenyl)-L-alanines **41** provides a one-step synthesis of optically active 3,4-dihydrocoumarins **42** (Eq. **39**).⁽⁹³⁾ The mechanistic pathway for this cyclization is similar to the one given in Eq. **8**. In this case, intramolecular bicyclization occurs involving nucleophilic attack by the carboxy group (**43** @ **44**) (Eq. **40**).



3.5. Intramolecular Carbon-Carbon Bond Formation

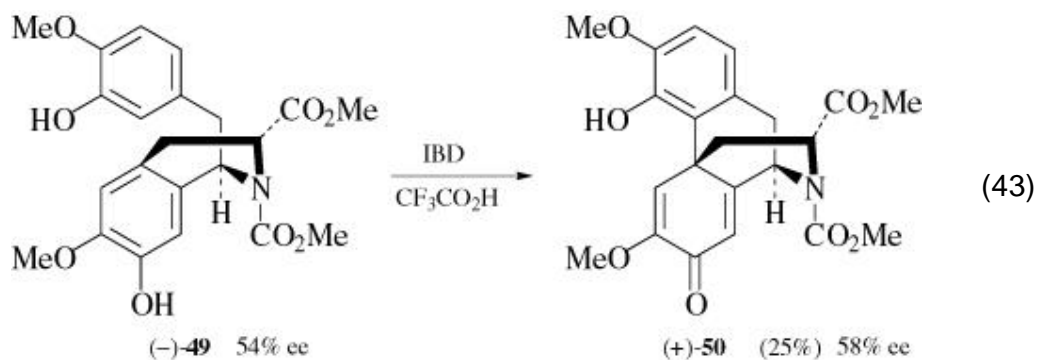
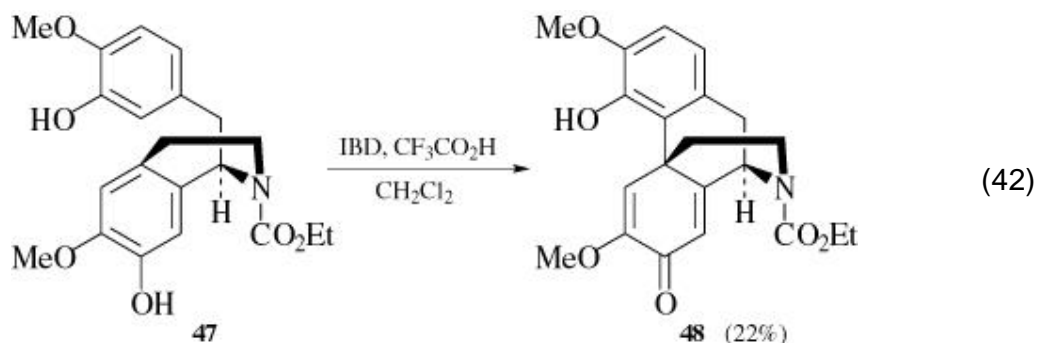
3.5.1. Phenolic Oxidative Coupling and its Synthetic Applications

A fascinating feature of hypervalent iodine reagents is their ability to effect oxidative carbon-carbon coupling of phenols. Such coupling is a key biosynthetic step to many natural products including several antibiotics and alkaloids. (5) A general mechanistic scheme for the coupling reaction is outlined in Eq. 41. This coupling process depends upon prior formation of an O-I(III) intermediate **45**, which can undergo intramolecular ortho-para or para-para carbon-carbon coupling (**45** \rightarrow **46**) upon reaction with a second equivalent of the phenol.

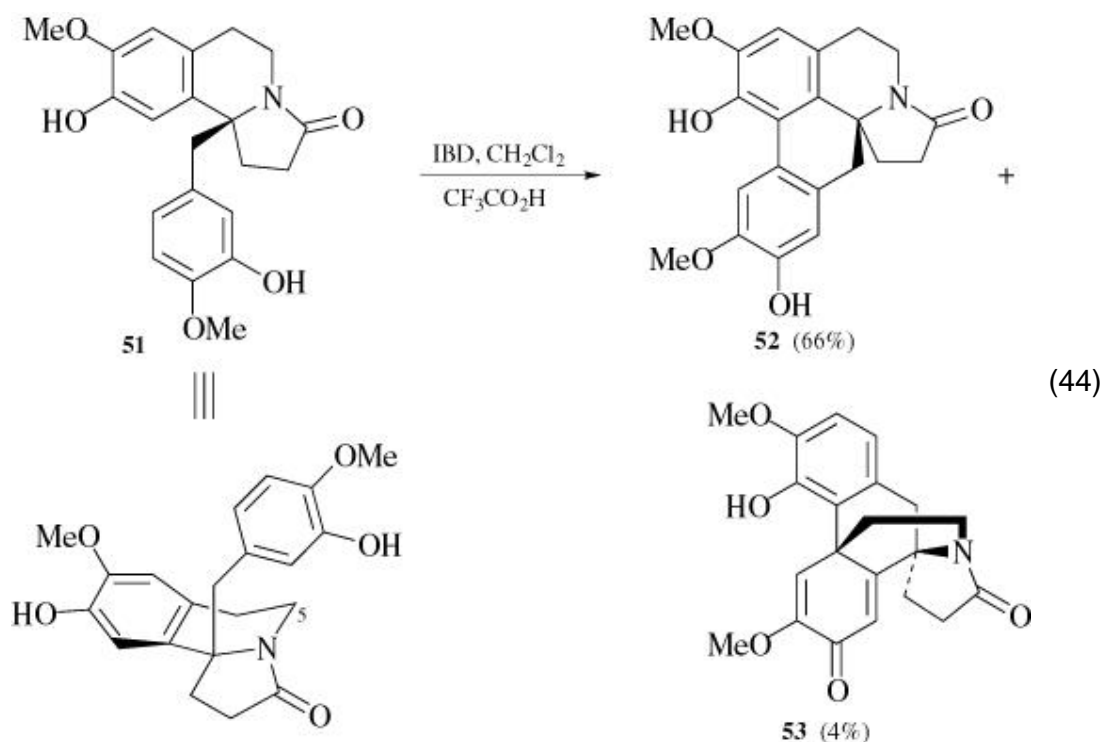


Phenolic oxidative coupling finds extensive use in biomimetic syntheses of a number of morphine alkaloids and analogs. (94–95) A key step in the biosynthetic pathway for morphine alkaloids is formation of salutaridine by

intramolecular oxidative cyclization of reticuline. (95) Various organohypervalent iodine reagents that have been used in the conversion of reticuline derivatives **47** to salutaridine derivatives **48** include IBD, IBTA, bis(trichloroacetoxy)iodobenzene, and different tetraethylammonium (acyloxy iodate) derivatives (Eq. 42). (96-98) This conversion involves ortho-para coupling with the creation of one new asymmetric center. A further noteworthy example of this approach is the asymmetric synthesis of (9*R*)-salutaridine derivative (+)-**50** from the oxidation of (-)-**49** (Eq. 43). (99)



Oxidation of conformationally rigid molecules such as bisphenol **51** with IBD gives a mixture of C-C coupling products related to aporphine (isoboldine analog **52**, major product) and morphinane alkaloids (**53**, minor product) (Eq. 44). (100)

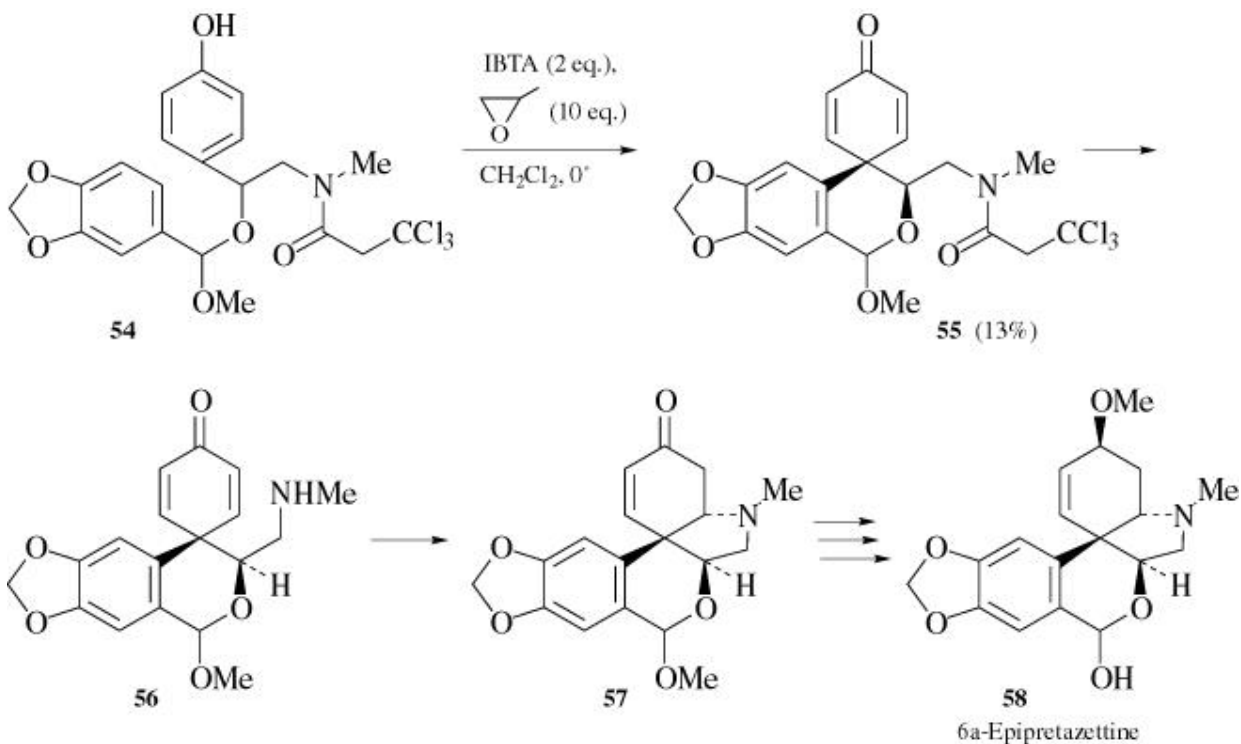


These results show that both coupling sites on the isoquinoline moiety are accessible to a pseudoaxial benzyl group. The larger percentage of isoboldine-type product **52**, which results from para-para coupling at the apparent expense of the ortho-para coupled product **53**, is likely the result of a steric factor. The benzyl group in an axial position may hinder the formation of ortho-para coupled product because of steric interaction with the C(5) hydrogens of the isoquinoline moiety.

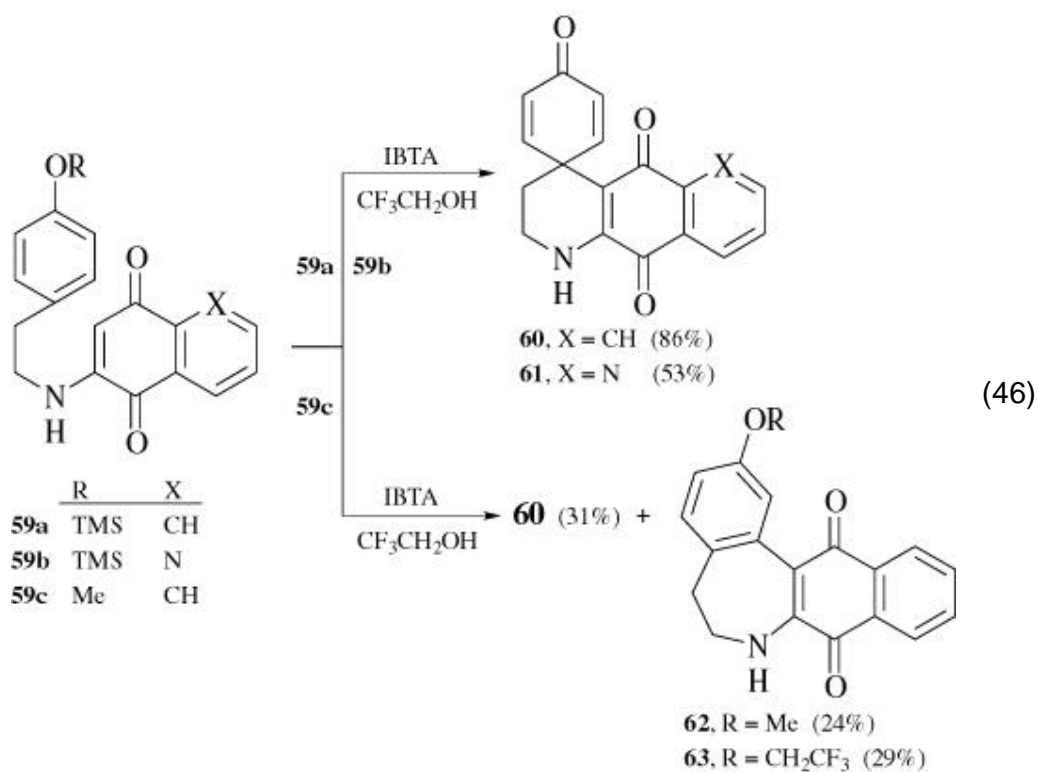
The phenolic oxidative coupling using IBTA as oxidant has been extended to the synthesis of 6a-epipretazettine (**58**) (Eq. 45). (101) The acetal **54** is converted to oxidative coupling product **55** with IBTA (2 equiv) in the presence of propylene oxide (10 equiv) in 13% yield. This step is followed by intramolecular Michael addition (**56** → **57**).

To control the selectivity of such oxidative coupling reactions, the starting phenols can be converted to the corresponding OTMS derivatives, which are subsequently oxidized to the desired products. Oxidation of *O*-silylated phenols **59a** and **59b** with IBTA in 2,2,2-trifluoroethanol (TFE) leads to the formation of azacarbocyclic spirodienones **60** and **61** in good yields. (102, 103) Oxidation of the corresponding methyl ether derivative **59c** under similar conditions affords a mixture of **60** and rearranged products **62** and **63** (Eq. 46).

(102) A remarkable use of this approach is the successful synthesis of the anticancer marine alkaloid discorhabdin C. (103, 104)

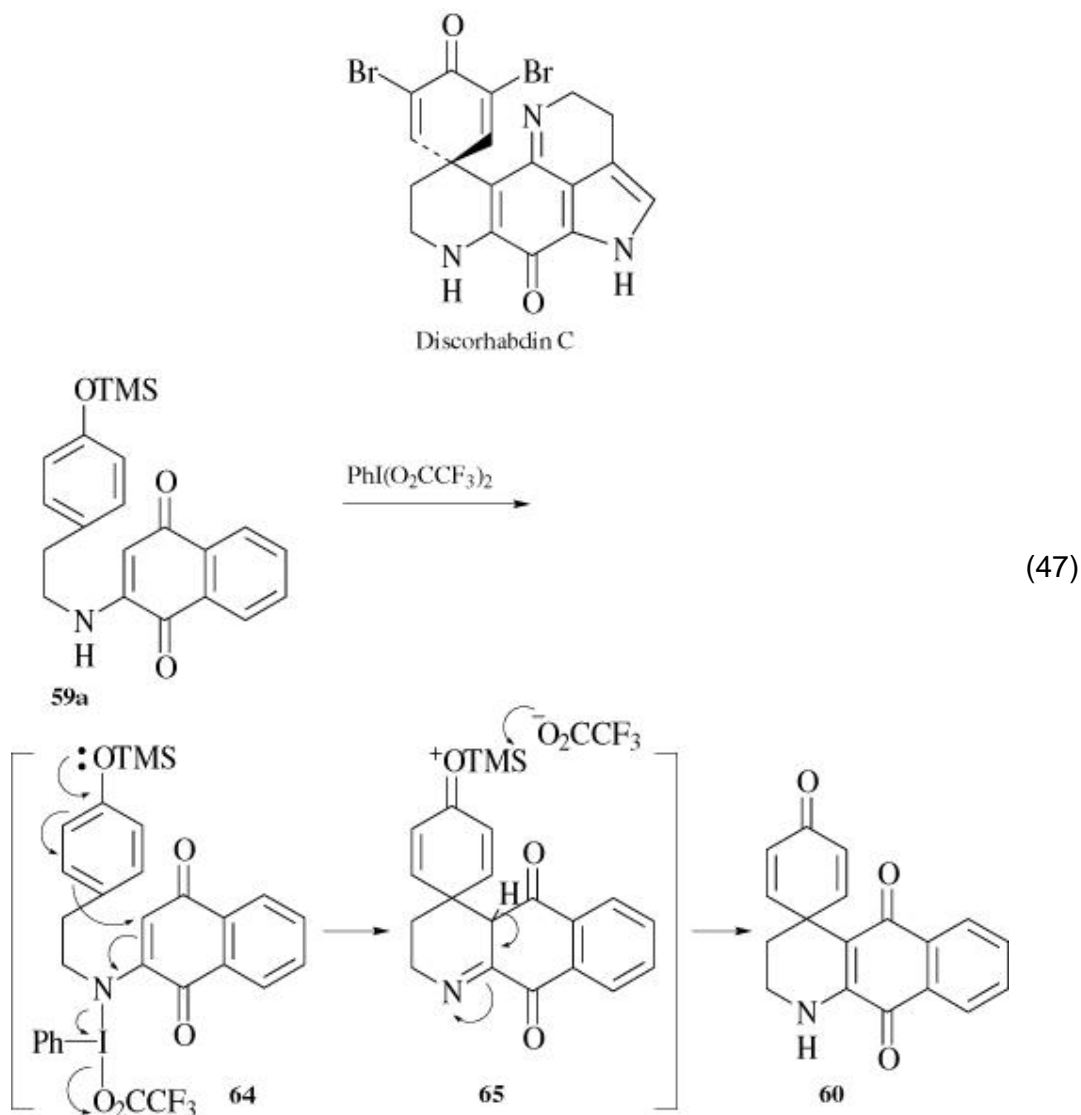


(45)



(46)

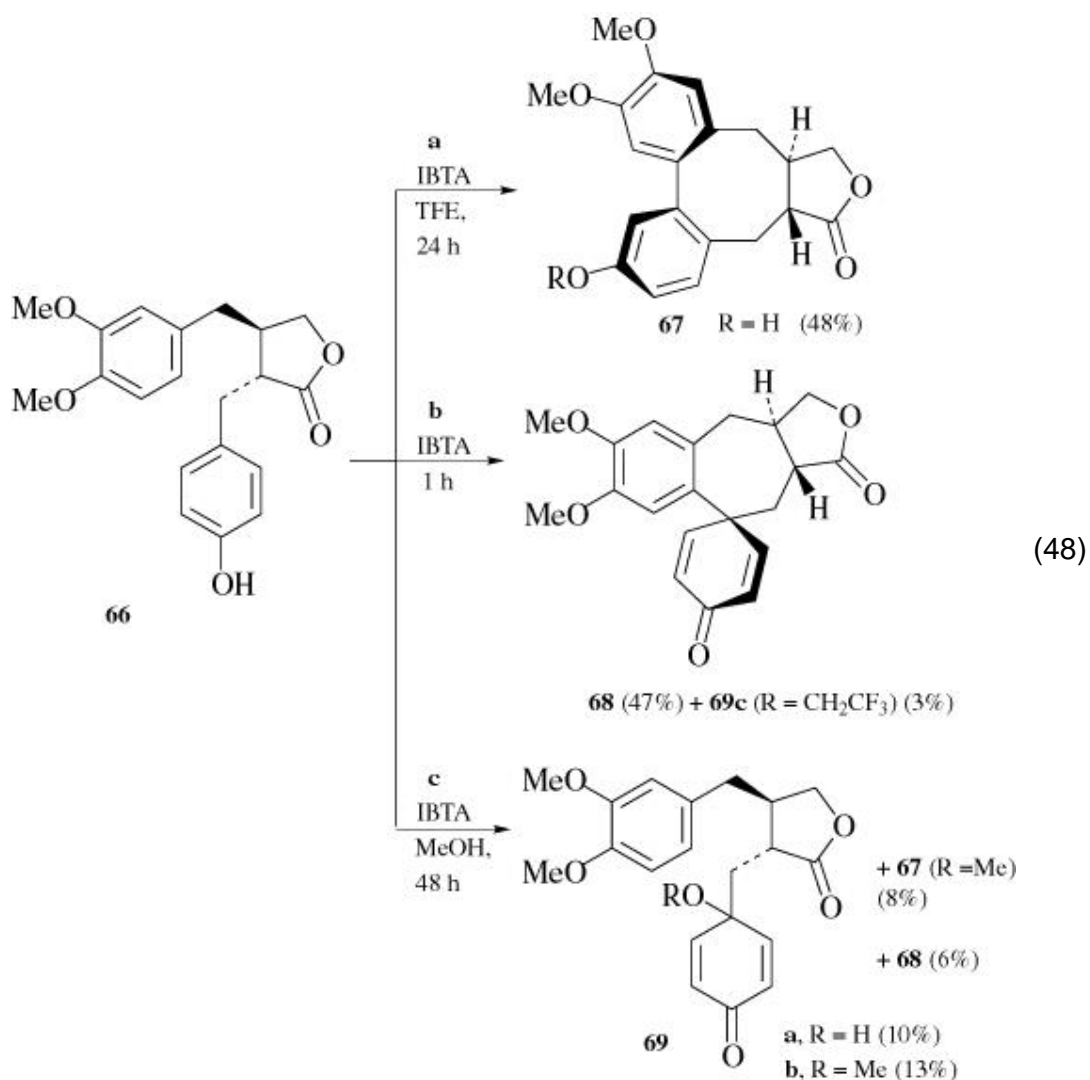
The conversion **59a** → **60** presumably proceeds by initial formation of an intermediate (**64** → **65**). The cleavage of the OTMS group by trifluoroacetate gives the product (**65** → **60**) (Eq. 47).

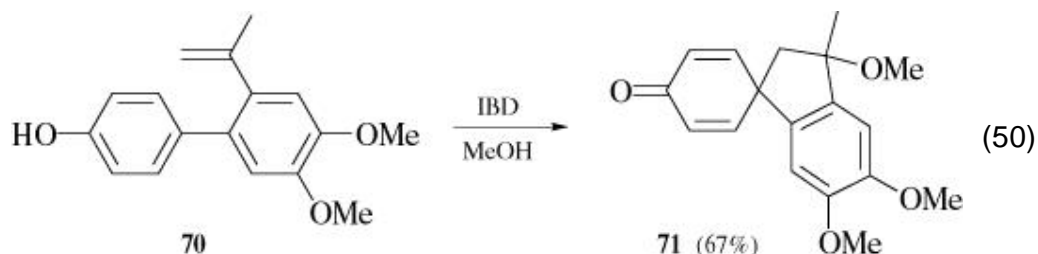
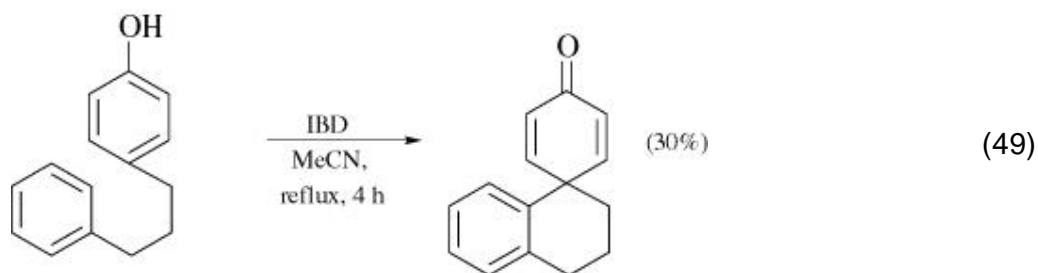


On oxidation with IBTA in TFE, phenolic dibenzylbutyrolactone **66** gives as the major product either the dibenzocyclooctadiene **67** (R = H) (Eq. 48, route **a**) or the spirodienone **68** (route **b**), depending upon the reaction time. When the reaction is left for 24 hours, the major product (48%) is **67** (R = H). When the reaction time is only 1 hour, the major product (47%) is **68** together with a

minor amount (3%) of the *p*-quinol monoether **69c**. The use of methanol instead of TFE in this reaction affords a mixture of products containing *p*-quinol **69a** and monoether **69b** in addition to **67** (R = Me) and **68** (route **c**). (105, 106) Route **a** of the oxidative cyclization has been employed to effect the asymmetric synthesis of isostegnane derivatives. (107)

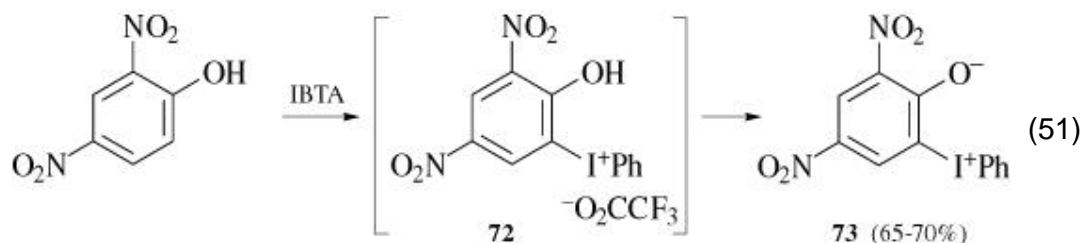
Intramolecular carbon-carbon bond formation is further exemplified by Eq. 49 in which the aromatic ring attacks the para position of the phenol ring. (108) The cyclization of styryl type systems (**70**→**71**, Eq. 50) is a logical extension of the process of Eq. 49. (66) However, there is a second mechanistic possibility involving initial attack of IBD at the styryl double bond.





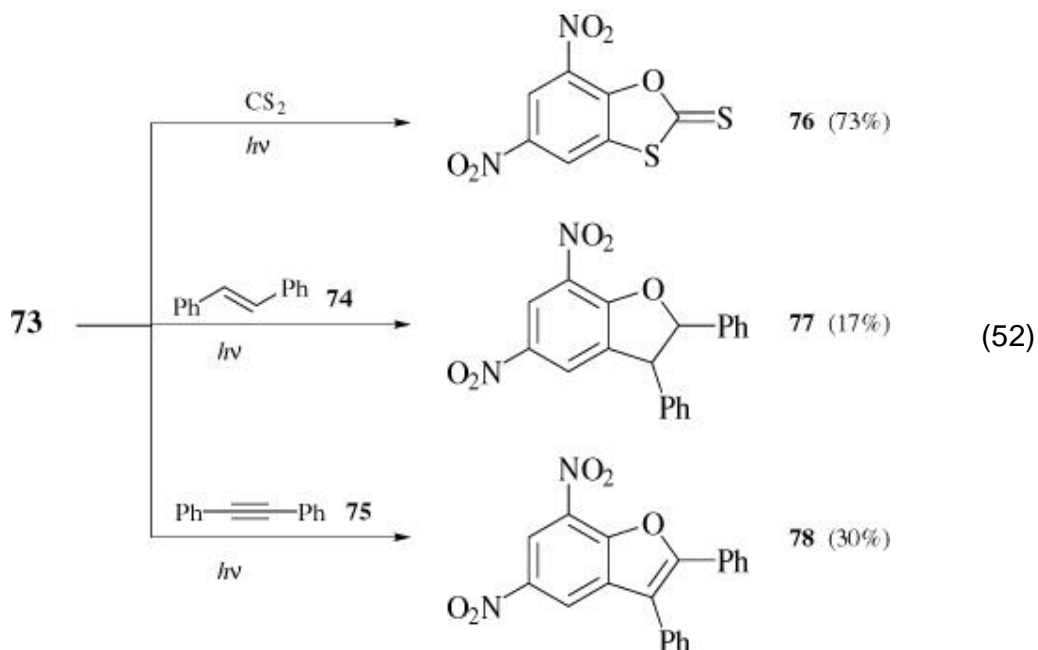
3.5.2. Formation of Iodonium Ylides and Salts and their Synthetic Applications

Phenols containing at least one electron-accepting group in the para position and one free ortho position react with organoiodine(III) reagents to yield stable iodonium ylides **73**. (109-112) The first step in ylide formation is the generation of iodine(III) intermediate **72** (iodonium salt). This subsequently loses trifluoroacetic acid under the influence of heat or base to give the stable ylide **73** (Eq. 51). (109) These iodonium ylides are important intermediates in the synthesis of heterocyclic compounds by cycloaddition reactions, in the formation of *o*-iodoethers by rearrangements, and in the formation of *o*-substituted phenols.

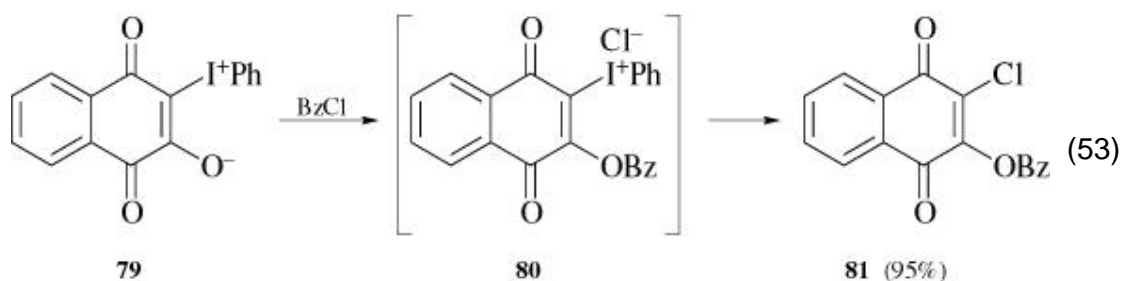


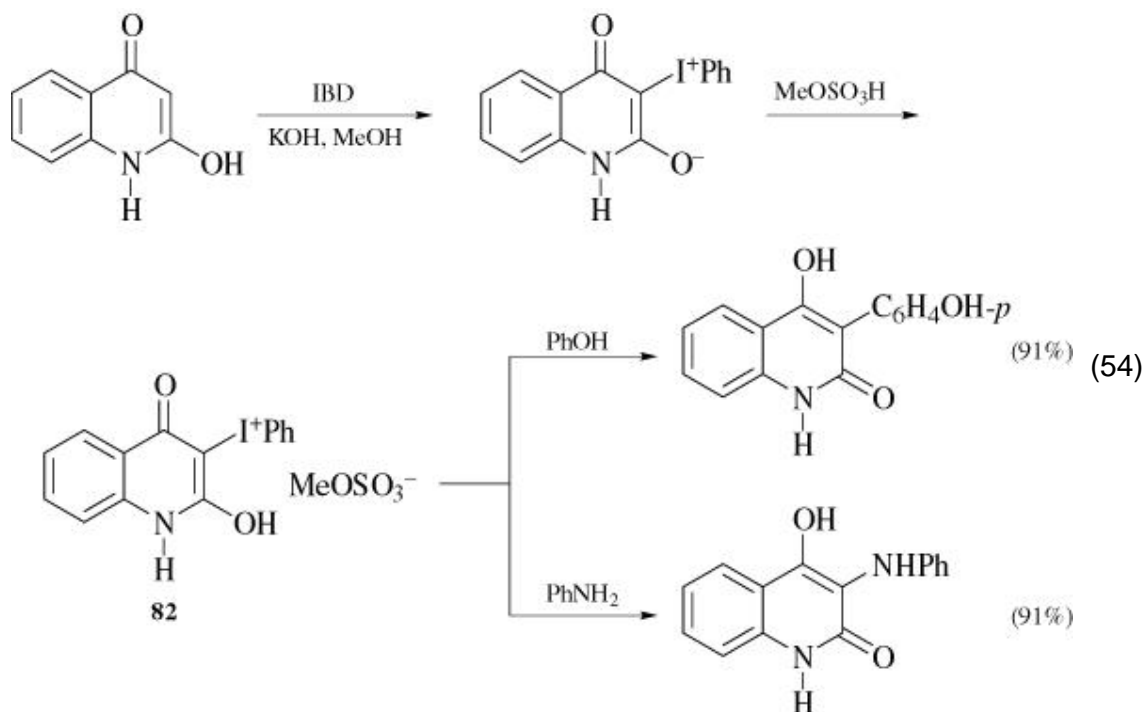
A variety of five-membered heterocyclic compounds can be synthesized by cycloaddition reactions of phenolic iodonium ylides with compounds containing double (113, 114) or triple bonds. (114, 115) The iodonium ylide **73** reacts

under photochemical conditions with carbon disulfide, alkene **74**, and alkynes **75** to afford 5,7-dinitro-1,3-benzoxathiole-thione (**76**), (**113**) 2,3-dihydrobenzo[*b*]furan **77**, (**114**) and benzo[*b*]furan **78**, (**114**) respectively (Eq. 52).

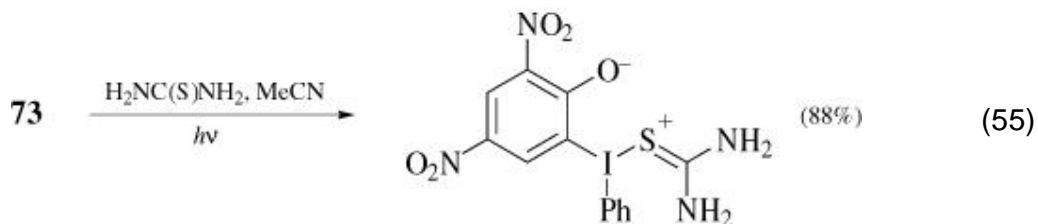


Another characteristic feature of iodonium ylides is their reaction with electrophiles to afford products bearing substituents in place of the phenyliodonium functionality. The electrophile first gives iodonium salts, which normally undergo subsequent nucleophilic substitution with the counteranion. For example, reaction of the ylide of 2-hydroxy-1,4-naphthoquinone (**79**) with benzoyl chloride produces 2-benzoyloxy-3-chloro-1,4-naphthoquinone (**81**) (Eq. 53). (**115**) The intermediate iodonium salt **80** could not be isolated. However, when the counteranion is not nucleophilic, it is possible to isolate the intermediate iodonium salts (e.g. **82**). In the presence of nucleophiles such as phenol and aniline, these salts can be converted to various functionalized phenolic compounds (Eq. 54). (**116**)

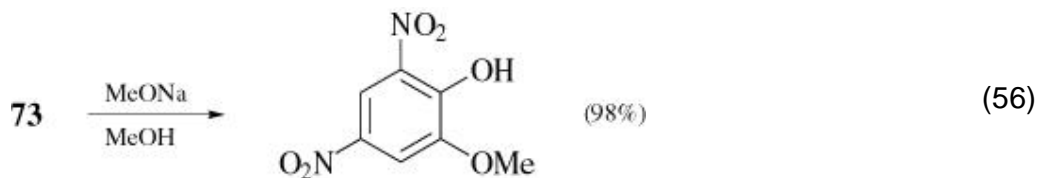




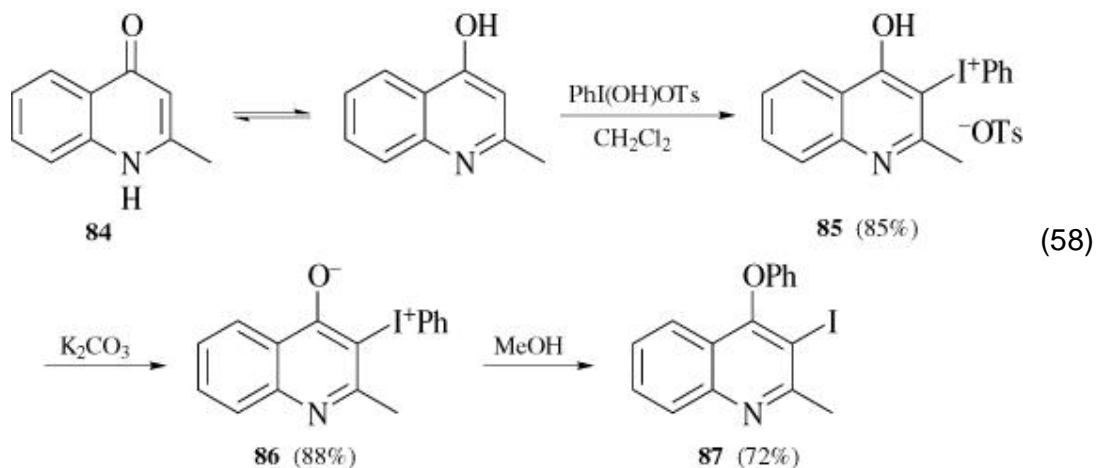
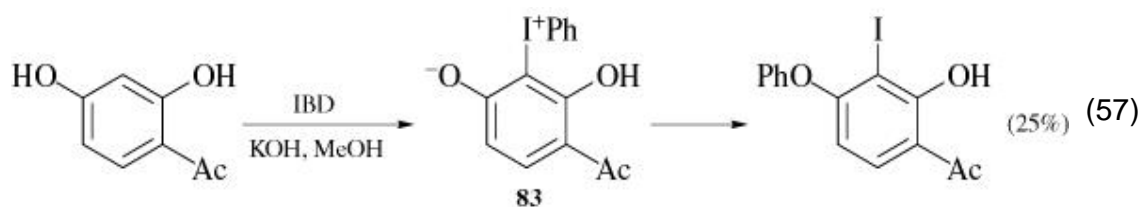
The iodonium ylides of phenols react with nucleophiles in two different ways. The first path outlined in Eq. 55 illustrates attack of the nucleophile on iodine to give an adduct. (117) This iodine adduct formation normally occurs under photo-chemical conditions.



The second path involves attack of a nucleophile at carbon, thereby giving the S_NAr substitution product with the expulsion of iodobenzene (Eq. 56). (118) Nonphotochemical reactions in the presence of strong nucleophiles favor a S_NAr substitution route.



Phenolic iodonium ylides undergo thermal 1,4-formal rearrangement to *o*-iodoaryl ethers. (110-122) Examples of such rearrangements are shown in Eq. 57 (112, 119) and Eq. 58. (120, 121) Equation 57 illustrates the rearrangement of phenolic ylide **83** containing an enolizable ketone, which remains unaffected in IBD- KOH/ MeOH. The conversions **84** @ **86** and **86** @ **87** represent the formation of the stabilized monocarbonyl iodonium ylide **86** and its rearrangement to iodoether **87** (Eq. 58). Intermediate iodonium salt **85** is also stable.

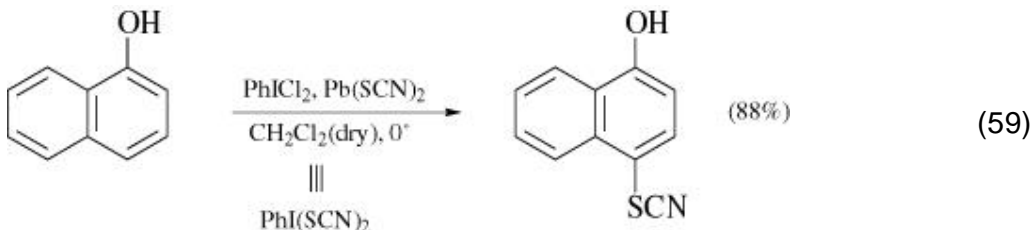


3.6. Miscellaneous

3.6.1. *p*-Thiocyanation of Phenols

A variety of phenols and α -naphthols undergo *p*-selective thiocyanation in the presence of (dichloriodo)benzene and lead dithiocyanate in dry

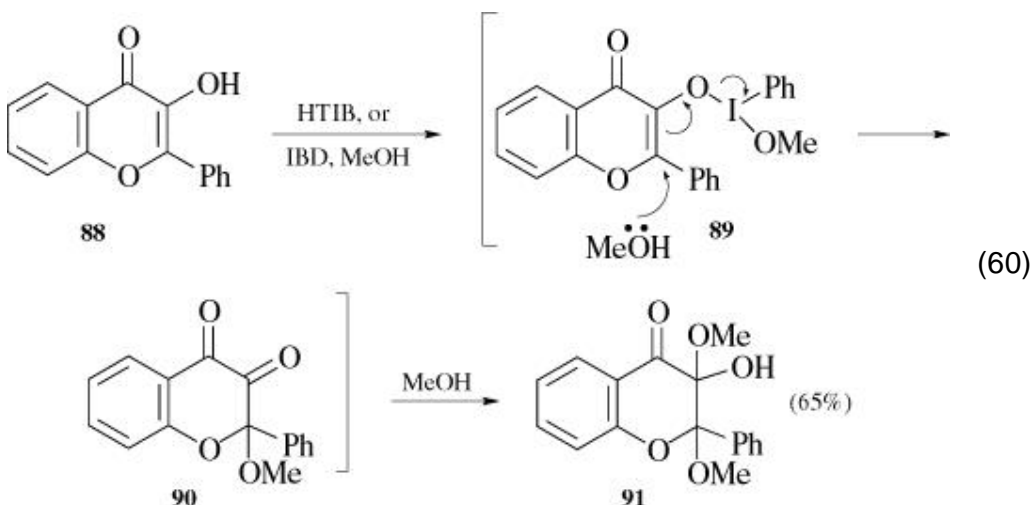
dichloromethane (Eq 59). The ligand exchange reaction of PhICl_2 and $\text{Pb}(\text{SCN})_2$ generates in situ [(bisthiocyanato)iodo]benzene, which effects the oxidation of the phenolic group analogously to other iodine(III) reagents such as IBTA or IBD.



The reaction is completed by the nucleophilic attack of thiocyanate anion at the para position. (123,123a)

3.6.2. Oxidation of Flavonols

Flavonols **88** behave like phenols upon oxidation with hypervalent iodine reagents. Thus, oxidation of **88** with HTIB or IBD in methanol proceeds with the introduction of two methoxy groups into the carbon-carbon double bond, thereby giving 2,3-dimethoxy-3-hydroxyflavanones **91** (Eq. 60). (124, 125) The use of periodic acid as an oxidant gives similar results. (126) Iodine(III) intermediate **89** of this reaction gives α -diketone **90** by Michael-type addition of methanol. The latter affords product **91** by nucleophilic addition of methanol at the C(3) position.

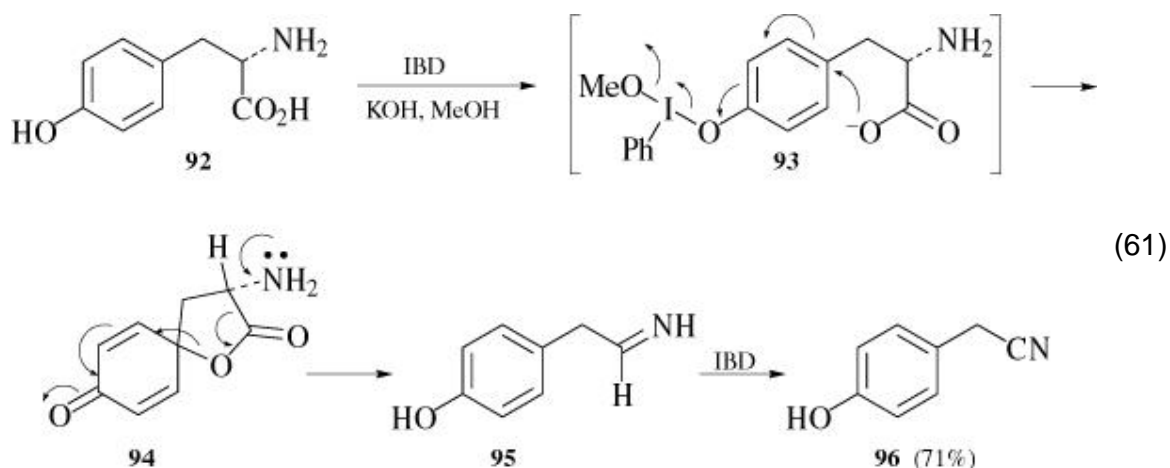


3.6.3. Cleavage of Amino-Terminal Tyrosyl-Peptide Bonds

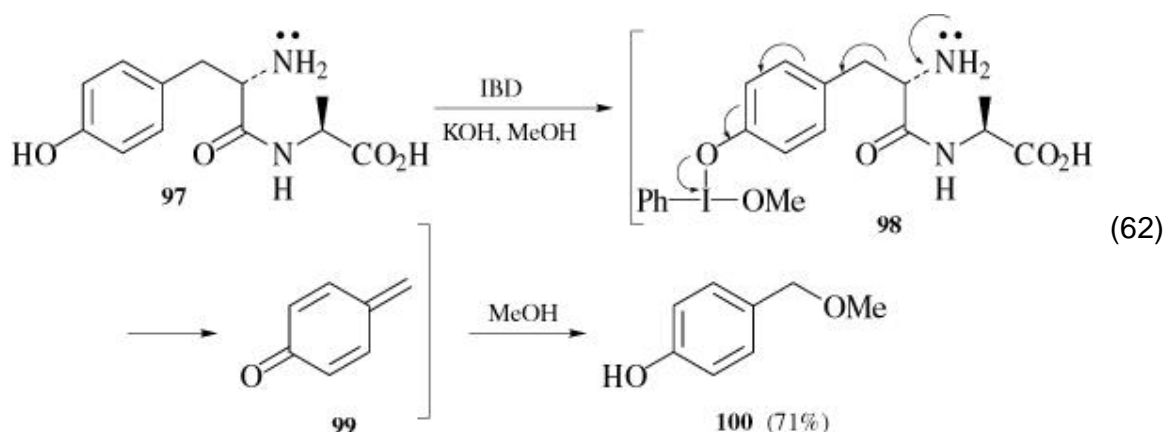
Tyrosine (**92**) (Eq. 61) and tyrosyl dipeptides **97** (Eq. 62) undergo cleavage of their carbon- NH_2 bonds when oxidized with IBD in methanol/potassium

hydroxide. (127) These reactions are explained on the basis of phenolic group oxidations discussed earlier. The first step of the reaction gives O-I(III) intermediate **93**, which then yields the spirolactone **94** by intramolecular participation of carboxylate anion. Decarboxylation followed by oxidation of the resulting imine **95** by the second molecule of IBD finally affords the cleavage product **96** (Eq. 61).

Cleavage of the amino-terminal tyrosyl-peptide bond in **97** also occurs via initial ligand exchange involving the phenolic hydroxy group and $\text{PhI}(\text{OMe})_2$ to give intermediate **98**. This intermediate undergoes reductive cleavage of iodobenzene via fragmentation initiated by the amino group, providing **99**.



Finally, nucleophilic attack of MeOH gives product **100** (Eq. 62). Cleavage of tyrosyl proteins using *o*-iodosobenzoic acid has also been reported. (128, 129)

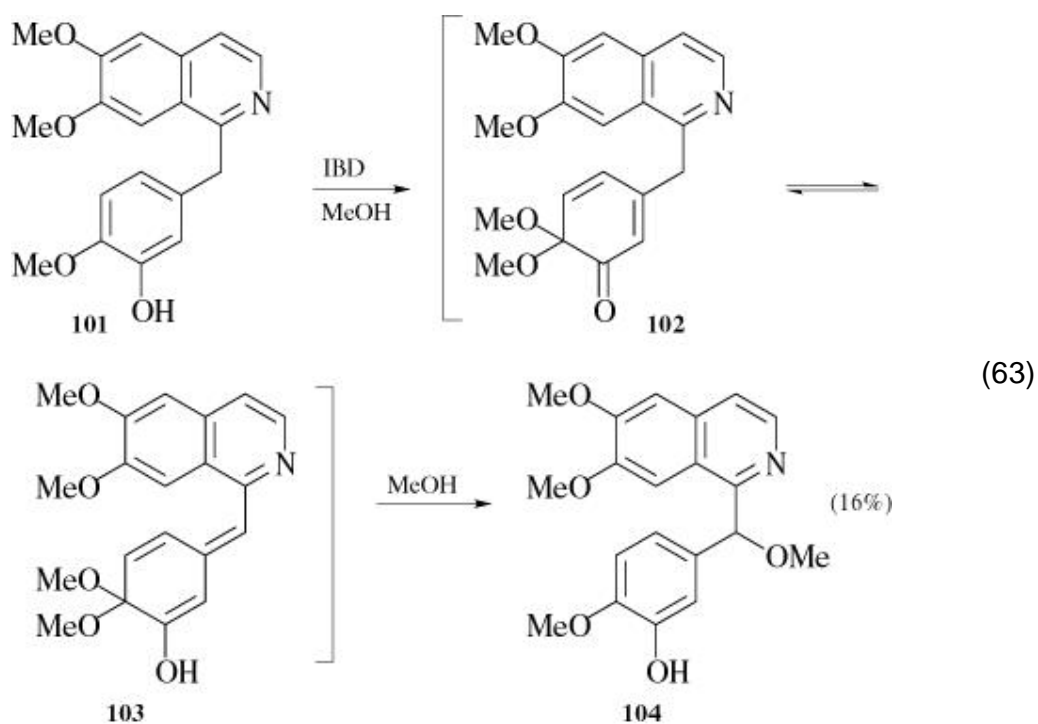


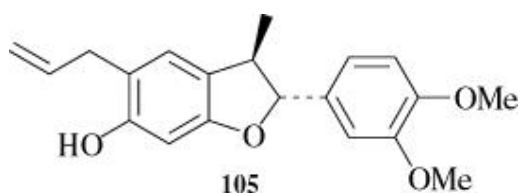
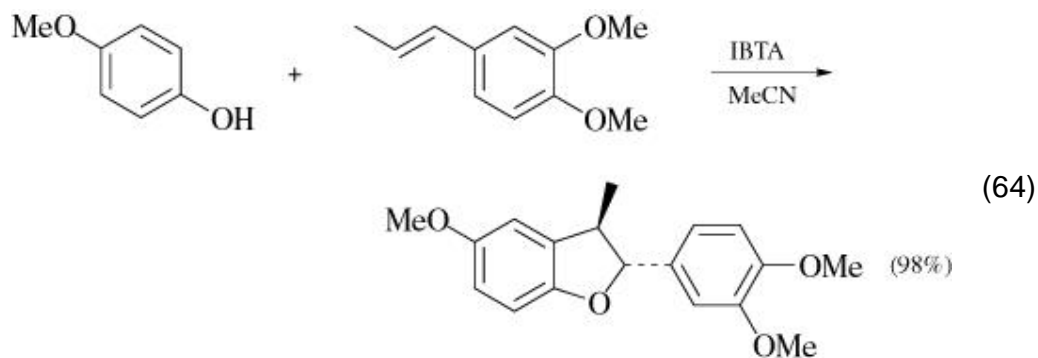
3.6.4. Oxidation of 3 ζ -Desmethylpapaverine

3 β -Desmethylpapaverine (**101**) on oxidation with two equivalents of IBD in methanol at room temperature gives a novel product **104** in 16% yield. (130) A possible pathway for this reaction involves the formation of *o*-quinone acetal **102** by oxidation of the phenolic group. This intermediate is converted to **103** which finally gives the product **104** by nucleophilic attack of methanol (Eq. 63).

3.6.5. Oxidative Phenol-Propenylbenzene Cycloadditions Leading to *trans*-2,3-Dihydrobenzofurans

Oxidation of various 4-methoxyphenols and naphthols with IBTA in the presence of electron-rich styrene derivatives such as 1,2-dimethoxy-4-propenylbenzene leads to formal cycloaddition of the alkene across the oxygen and C(2) of the phenol, thereby affording a *trans*-dihydrobenzofuran structure related to the neolignan family of natural products (Eq. 64). (131) This reaction permits a facile preparation of **105**, which can be converted to (\pm)-kadsurenone and (\pm)-denudatin B. Similar cycloaddition reactions have also been effected by using electrochemical methods.

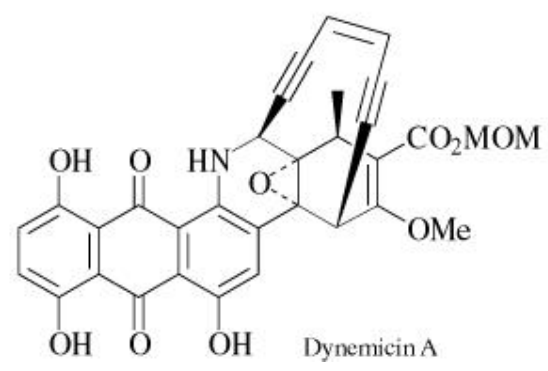
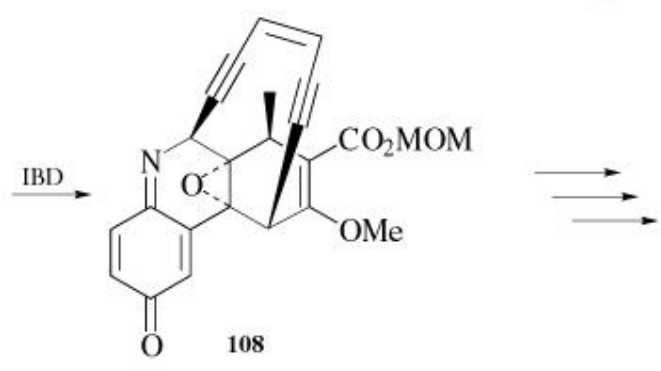
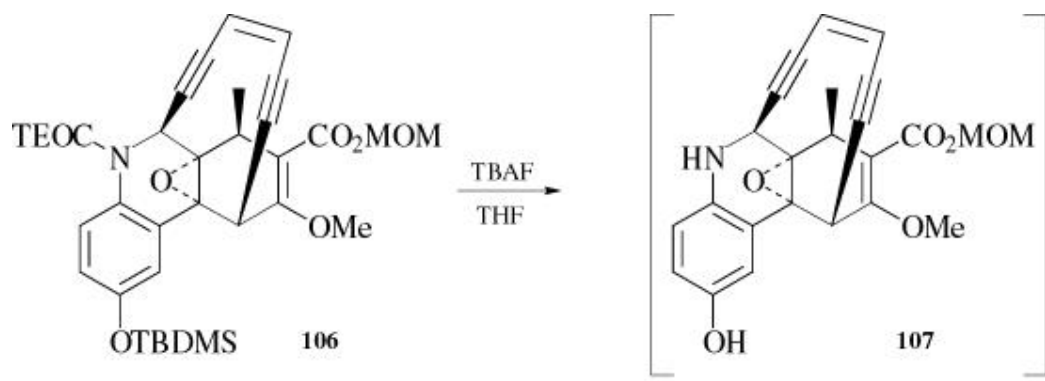




However, for the reaction of 2-naphthol and propenylbenzene, anodic oxidation gives a much lower yield of the product compared to IBTA oxidation.

3.6.6. Synthesis of Dynemicin A

Iodine(III)-induced oxidative conversion of phenols to quinone imines has been employed in the total synthesis of dynemicin A, a metabolite isolated from *Micromonospora chersina*, which has DNA cleaving capability and demonstrated in vitro antitumor properties. Phenolic intermediate **107**, generated in situ by removal of some of the protecting groups from **106**, undergoes oxidation to quinone imine **108** with IBD (Eq. 65). (132) Compound **108** is the key intermediate for subsequent elaboration to dynemicin A.

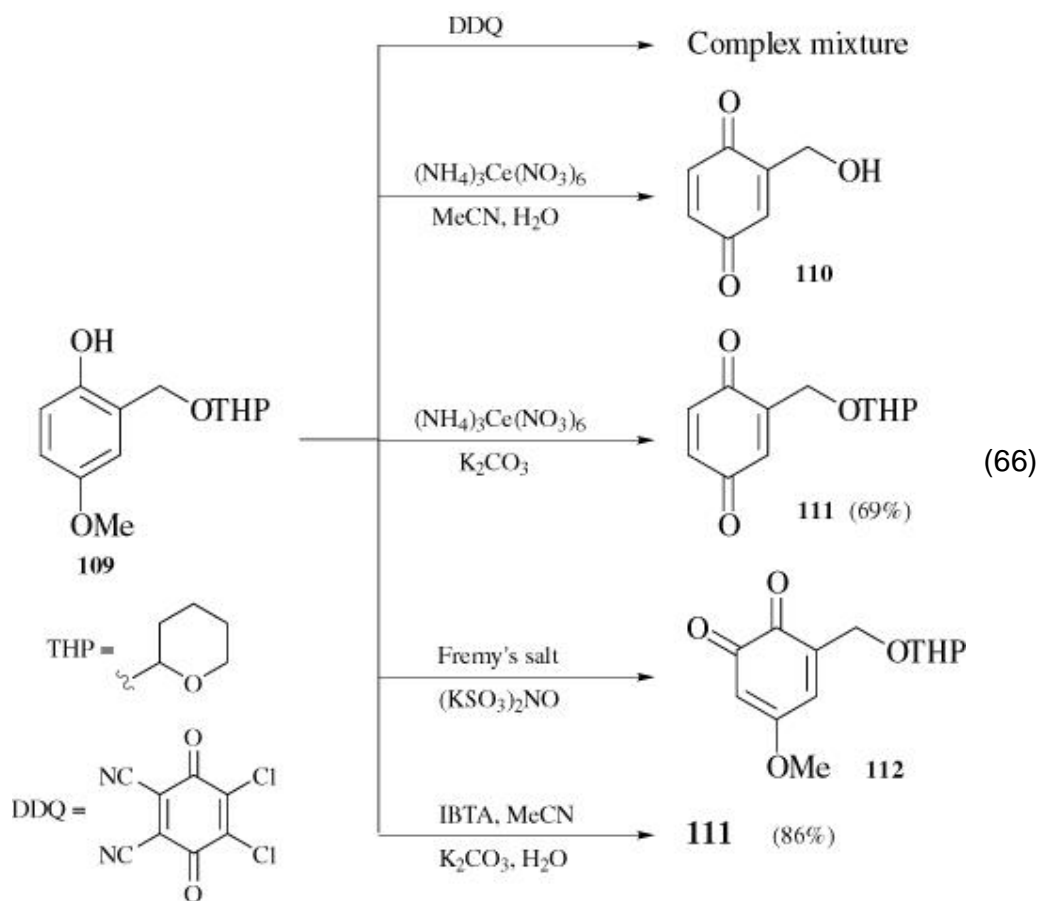


4. Comparison with Other Methods

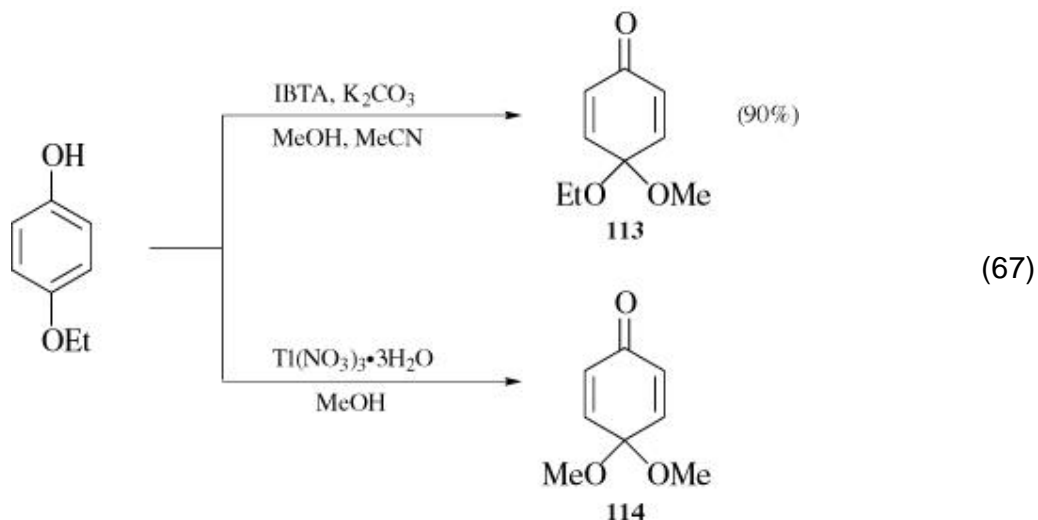
There are several alternative methods for effecting most of the major processes reviewed in this chapter with the exception of ylide formation, which is a unique property of organohypervalent iodine reagents. In most cases, organohypervalent iodine based methodology is more effective owing to its ease, simplicity, selectivity, and efficiency. However, hypervalent iodine-mediated oxidations do have some limitations, such as low yields of products in a few cases and relatively high cost of the organohypervalent iodine reagents (although the iodobenzene generated as byproduct of the reaction can be recycled). Some examples of direct comparison of iodine(III)-based reactions with other common methods are presented according to the type of reaction accomplished.

4.1.1. Oxidation of Phenols to Quinones and Related Compounds

Quinones, quinone monoacetals, and related compounds are generally prepared by (1) chemical oxidation of phenols or 4-alkoxyphenols with various metal oxidants, (133, 134) Fremy's salt, (13) silver oxide, (135-138) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); (139) (2) electrochemical oxidation of 4-methoxyphenols (140-142) or their trimethylsilyl ethers; (143) or (3) monohydrolysis of bis(acetals). (144) Although the first group of reagents offers the most facile and shortest route to quinones and their derivatives, there are some limitations, especially with phenols that have acid-sensitive groups. For example, oxidation of 4-methoxy-2-(tetrahydropyranyloxy)methylphenol (109) with various oxidizing agents is problematic. While oxidation of 109 with DDQ in methanol gives a complex mixture, use of ammonium ceric(IV) nitrate (145) in the presence of water or potassium carbonate, respectively, results in the formation of the *p*-quinone alcohol 110 or the desired *p*-quinone 111, but in unsatisfactory yield (69%). With Fremy's salt in potassium dihydrogen phosphate solution, oxidation of 109 does not give *p*-quinone 111 but rather *o*-quinone 112. Since oxidation of 109 to 111 has been most effectively accomplished by using IBTA in acetonitrile/water in the presence of potassium carbonate, the I(III) method is obviously advantageous. Of course, the use of other oxidants may serve as a complementary approach for a specific purpose (e.g. 109 to 112) (Eq. 66).

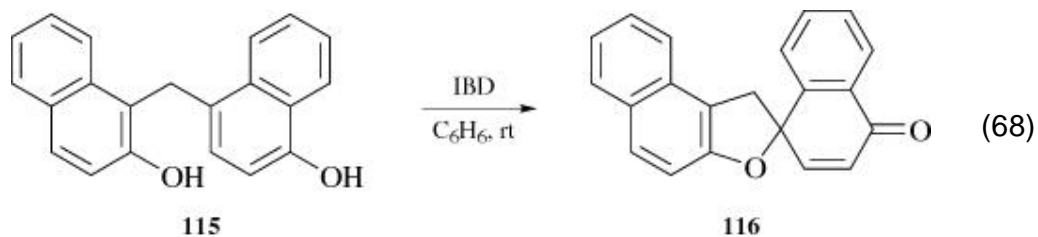


Another example of phenolic oxidation where an I(III) reagent is of special interest is the formation of unsymmetrical monoacetals **113** in the reaction of *p*-alkoxyphenols with IBTA in methanol. This result is quite different from that observed in thallium trinitrate oxidation, (17, 146) which gives the symmetrical dimethylacetal **114** (Eq. 67).



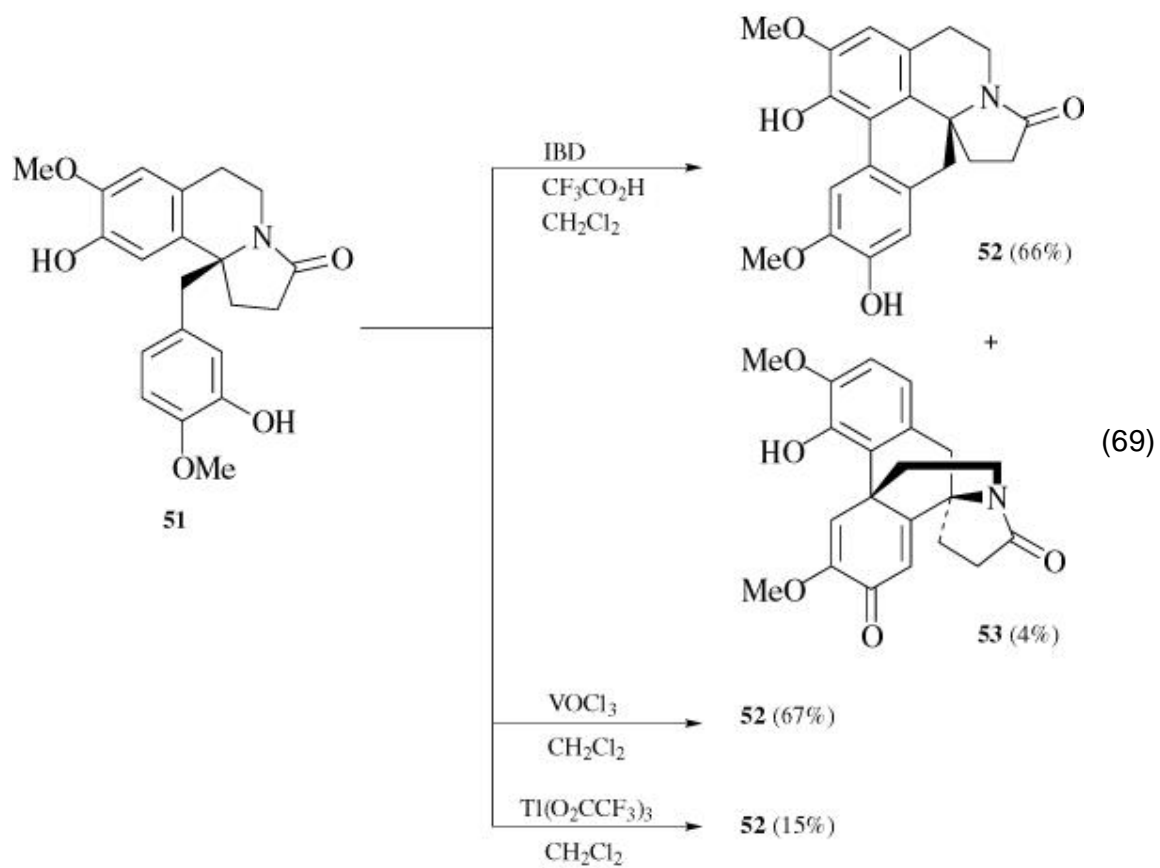
4.1.2. Intramolecular Participation in the Oxidation of Phenols

Of the various examples of the oxidative cyclization involving intramolecular participation of oxygen or nitrogen, one that deserves special comment is the conversion of bisnaphthol **115** to spiran **116**. In this reaction, no oxidizing agent except IBD is successful (Eq. 68). (74)



4.1.3. Intramolecular Carbon-Carbon Bond Formation: Phenolic Oxidative Coupling

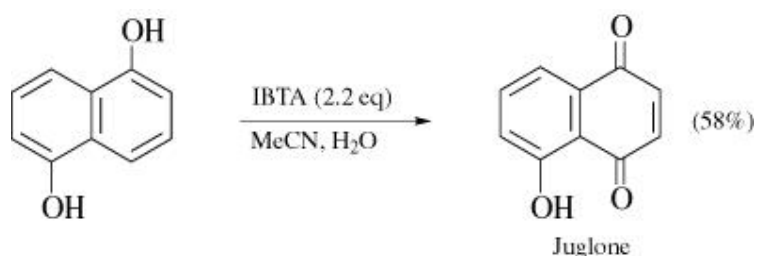
Intramolecular C-C bond formation in phenolic oxidation using I(III) reagents provides a nonmetallic and safer alternative to existing methods, although yields in most reactions are low. The study of the oxidation of conformationally rigid 1-benzyltetrahydroisoquinolines **51** (Eq. 44) with various oxidizing agents show that IBD and vanadium oxychloride may be the reagents of choice for preparing aporphine-type products **52**. Oxidation of **51** with thallium(III) trifluoroacetate gives **52** in very low yield (15%). The morphinane-type product **53** is available only from IBD oxidation, although the yield is very poor (4%) (Eq. 69). (100)



5. Experimental Procedures

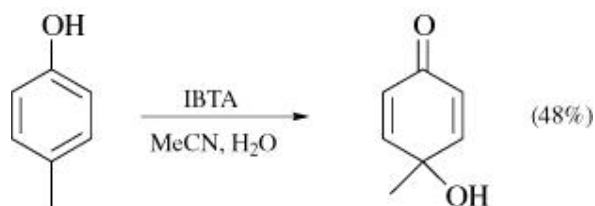
5.1.1. Practical Aspects and Availability of Organohypervalent Iodine Reagents

All organohypervalent iodine reagents are solids that are fairly stable at room temperature and generally insensitive to atmospheric oxygen and moisture. Most reagents have relatively low toxicity and can be handled easily. IBD, (147-150) IBTA, (151) and HTIB (152, 153) are stable and commercially available, or can be prepared by standard procedures. Iodosobenzene (149) can be prepared by hydrolysis of either (dichloriodo)benzene (149) or IBD and should be stored in a refrigerator in dark containers. The preparation of iodine(V) reagent iodylbenzene can best be effected by direct oxidation of iodobenzene with aqueous hypochlorite and phase-transfer reagents. (154)



5.1.2. 5-Hydroxy-1,4-naphthoquinone (Juglone) [Oxidation of a Phenol to a *p*-Quinone] (50)

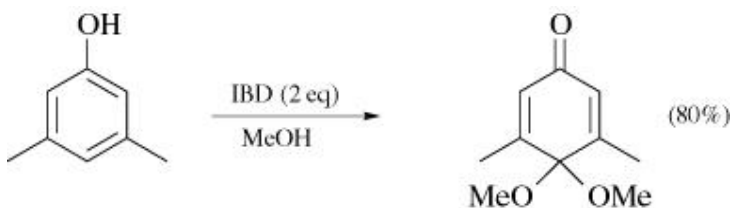
A solution of 1,5-dihydroxynaphthalene (160 mg, 1 mmol) in acetonitrile-water (2/1, v/v) (12 mL) was added dropwise to [bis(trifluoroacetoxy)iodo]benzene (IBTA)-(946 mg, 2.2 mmol). The resulting solution was stirred at 0° under nitrogen for one hour. The solvent was removed in vacuo, and the resulting residue was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were dried (MgSO₄) and evaporated in vacuo to yield the crude product, which was purified by column chromatography to give 101 mg (58%) of pure juglone, mp 154–155°; IR 1645, 1670, 3300–3600 cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 6.8 (s, 2 H), 7.2 (m, 1 H), 7.5 (s, 2 H).



5.1.3. 4-Hydroxy-4-methylcyclohexa-2,5-dienone [Oxidation of a *para*-Substituted Phenol to a *p*-Quinol] (62)

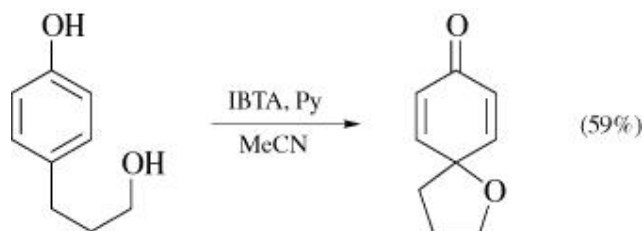
To a stirred solution of *p*-cresol (108 mg, 1 mmol) in acetonitrile-water (3/1, v/v) (4 mL) was added IBTA (473 mg, 1.1 mmol) at 0° and stirring was continued for about 15 minutes. The reaction was quenched by addition of water (4 mL) and the resulting mixture was extracted with dichloromethane (4 × 5 mL). The combined organic extracts were dried (Na₂SO₄) and evaporated under reduced pressure to give a brown residue, which was purified by column chromatography on silica gel (ether-light petroleum) to give 60 mg (48%) of the title product as colorless needles, mp 75–77° (from CHCl₃-hexane); ¹H NMR (CDCl₃, 60 MHz) δ 1.44 (s, 3 H), 3.48 (bs, 1 H), 6.05 (d, *J* = 10 Hz, 2 H), 6.89 (d, *J* = 10 Hz, 2 H).

The same procedure was used for effecting the oxidation of tripropylsilyl ethers of *para*-substituted phenols to *p*-quinols. Oxidations required 0.5–2.0 hours.



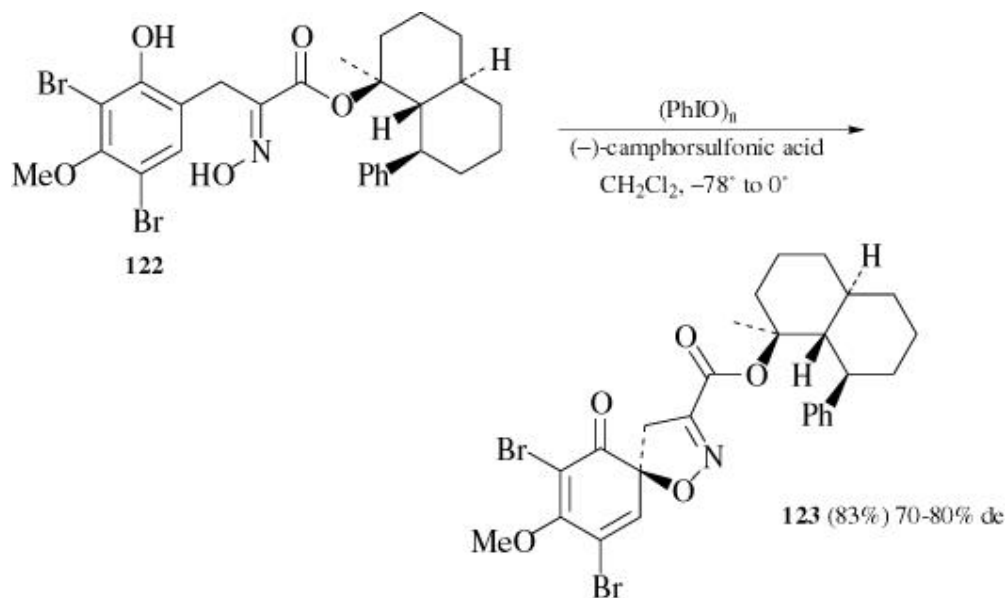
5.1.4. 4,4-Dimethoxy-3,5-dimethylcyclohexa-2,5-dienone [Oxidation of a *Monophenol* to a *p*-Quinone Monoacetal] (53)

To a stirred solution of 3,5-dimethylphenol (620 mg, 5 mmol) in dry methanol (10 mL) was added dropwise at room temperature a solution of iodobenzene diacetate (IBD) (3.22 g, 10 mmol) in methanol (25 mL) via a double-ended needle. The solution became reddish and was stirred under nitrogen for about 40 minutes. Methanol was removed in vacuo to give a yellow oil, which was purified by column chromatography on silica gel (230–40 mesh) using light petroleum (bp 40–60°)-dichloromethane as eluants to afford 728 mg (80%) of the title product as colorless prisms, mp 59–61°; IR (KBr) 1650, 1685 cm⁻¹; ¹H NMR (CDCl₃) δ 1.9 (s, 3 H), 3.02 (s, 6 H), 6.28 (s, 2 H); ¹³C NMR (CDCl₃) δ 16.2, 50.8, 98.1, 131.8, 155.0, 184.7; MS *m/z* 182 (0.5), 167 (100), 135 (33), 127 (41), 123 (53).



5.1.5. 1-Oxaspiro[4,5]deca-6,9-dien-8-one [Formation of a Spiroquinone by Intramolecular Participation of a Primary Alcoholic Group] (84)

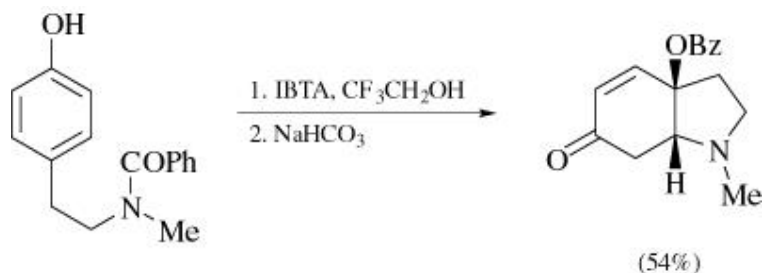
To a stirred solution of *p*-(3-hydroxypropyl)phenol (152 mg, 1 mmol) and pyridine (0.3 mL) in acetonitrile (10 mL) at 0° was added a solution of IBTA (430 mg, 1 mmol) in acetonitrile (2 mL). The mixture was stirred at room temperature for 10 minutes, diluted with water, and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with saturated aqueous sodium chloride solution, dried (MgSO₄), and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexanes-ethyl acetate to give 89 mg (59%) of the title product as a syrup; IR (CHCl₃) 1630, 1670, 1690 cm⁻¹; ¹H NMR (CDCl₃) δ 2.0–2.4 (m, 4 H), 4.06 (t, *J* = 6 Hz, 2 H), 6.08 (d, *J* = 10 Hz, 2 H), 6.76 (d, *J* = 10 Hz, 2 H).



5.1.6. (1*S*,8*R*,9*R*,10*R*)-1'-Methyl-8*c*-phenyl-1'-decalyl 7,9-Dibromo-8-methoxy-6-oxo-1-oxa-2-azaspiro[4.5]deca-2,7,9-triene-3-*c*

arboxylate [Asymmetric Induction in the Oxidative Cyclization of an *o*-Phenolic Oxime Ester] (86, 87)

(–)-Camphorsulfonic acid (1.28 g, 5.5 mmol) was added to a suspension of iodosobenzene (1.22 g, 5.5 mmol) in dichloromethane (60 mL) at room temperature and the mixture was stirred for 2 hours. The resulting clear solution was cooled to -78° and a solution of *o*-phenolic oxime-ester **122** (3.06 g, 5 mmol) in dichloromethane (60 mL) was added. The mixture was allowed to warm to 0° . After addition of water, the mixture was stirred for 30 minutes at room temperature and extracted with diethyl ether (3×100 mL). The combined extracts were dried (MgSO_4) and concentrated in vacuo. The residue was purified by column chromatography on silica gel using benzene as eluant to afford 2.53 g (83%) of **123** [70–80% de; the diastereomeric excess was estimated on the basis of the 500-MHz ^1H NMR spectrum (CDCl_3), in which a peak due to a vinyl proton (10-H) of each diastereomer appears as a singlet at δ 6.71 and 6.67 (91:1)]; mp 175 – 177° ; IR (CHCl_3) 1600, 1710, 2590, 3370 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.46 (s, 3 H), 1.21–1.80 (m, 12 H), 2.10–2.94 (m, 3 H), 2.17 (major product) (d, $J = 17.6$ Hz, 1 H), 3.00 (major product) (d, $J = 17.6$ Hz, 1 H), 2.72 (minor product) (d, $J = 17.7$ Hz, 1 H), 2.86 (minor product) (d, $J = 17.7$ Hz, 1 H), 4.15 (s, 3 H), 6.65 (major product) (s, 1 H), 6.66 (minor product) (s, 1 H), 7.1–7.3 (m, 5 H); ^{13}C NMR (CDCl_3) (major product) δ 21.2, 22.9, 26.3, 33.8, 34.5, 37.1, 37.7, 40.7, 44.4, 46.5, 49.6, 62.0, 86.7, 90.4, 107.2, 119.1, 125.6, 127.8, 128.4, 137.1, 147.3, 150.9, 157.2, 163.1, 188.9; MS (FAB) m/z 609 ($\text{M}^- + 4$), 607 ($\text{M}^- + 2$), 605 (M^-).



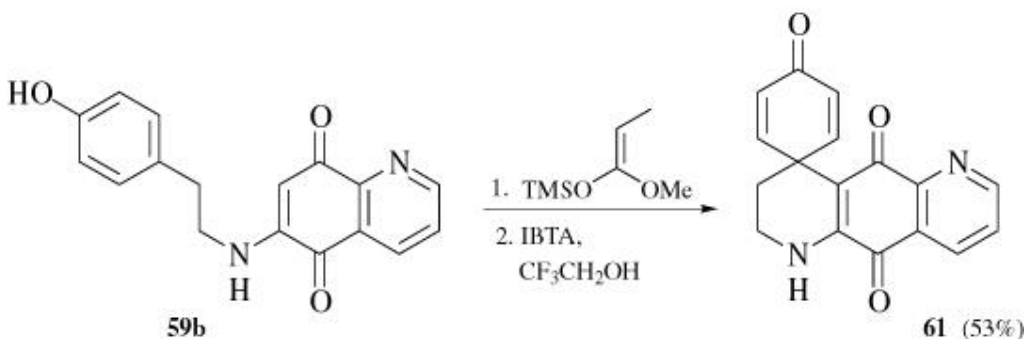
5.1.7. 1-Benzoyloxy-7-methyl-*cis*-azabicyclo[4.3.0]non-2-en-4-one [Formation of a Hexahydroindol-6-one by Oxidation of an *N*-Alkyl-*N*-benzoyltyramine] (67)

To a solution of *N*-methyl-*N*-benzoyltyramine (21.1 mg, 0.08 mmol) in trifluoroethanol (1 mL) was added IBTA (43 mg, 0.1 mmol). The mixture was stirred at room temperature for 30 minutes and then neutralized with solid sodium bicarbonate. The mixture was concentrated in vacuo and the resulting residue was dissolved in ethyl acetate and filtered. The filtrate was evaporated in vacuo and the residue was purified by column chromatography on silica gel to give 12.1 mg (54%) of pure product as a hygroscopic colorless oil; IR 1600,

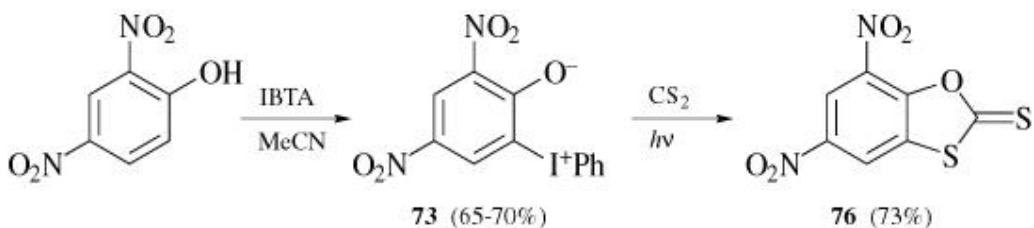
1685, 1715 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 2.3–2.4 (m, 1 H), 2.34 (s, 3 H), 2.4–2.55 (m, 2 H), 2.71 (dd, $J = 2, 17$ Hz, 1 H), 2.95–2.99 (m, 1 H), 3.05 (m, dd, $J = 5, 17$ Hz, 1 H) 3.1–3.2 (m, 1 H), 6.03 (d, $J = 10$ Hz, 1 H), 7.06 (dd, $J = 2, 10$ Hz, 1 H), 7.46 (t, $J = 7$ Hz, 2 H), 7.59 (t, $J = 7$ Hz, 1 H), 8.01 (d, $J = 8$ Hz, 2 H); HRMS 271.1204.

5.1.8. 5,6,7,8,9,10-Hexahydropyrido[2,3-g]quinoline-5,10-dione-9-spiro-4'-cyclohexa-2', 5'-dien-1'-one (61) [Oxidative Cyclization of an O-Silylated Phenol to an Azacarboyclic Spirodienone] (104)

To a stirred suspension of 6-[2-(4-hydroxyphenyl)ethylamino]quinoline-5,8-dione (26.5 mg; 0.900 mmol) in dichloromethane (4 mL) was added dropwise *O*-trimethylsilyl ketene acetal (75 mg, 0.469 mmol) at room temperature over 3 hours under nitrogen. The mixture was concentrated in vacuo to give the *O*-silylated phenol of **59b**, which was dissolved in 2,2,2-trifluoroethanol (5 mL). To the resulting solution was added IBTA (46.5 mg, 0.108 mmol).



After 15 minutes, the reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography to give 14 mg (53%) of azacarboyclic spiro dienone **61** as a red crystalline solid, mp 235–237° (from chloroform-hexanes); UV (MeOH) 231 (ϵ 24, 400), 249 (21,100), 464 (2640) nm; IR 1600, 1660, 3400 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.98 (t, $J = 6$ Hz, 2 H), 3.60–3.68 (m, 2 H), 6.33 (br s, 1 H), 6.39 (d, $J = 10$ Hz, 2 H), 6.92 (d, $J = 10$ Hz, 2 H), 7.55 (m, 1 H), 8.34 (d, $J = 8$ Hz, 1 H), 8.97 (d, $J = 4$ Hz, 1 H).



5.1.9. 5,7-Dinitro-1,3-benzoxathiole-2-thione [Synthesis of an Oxathiole by Photochemical Decomposition of a Phenolic Iodonium Ylide in the Presence of Carbon Disulfide]

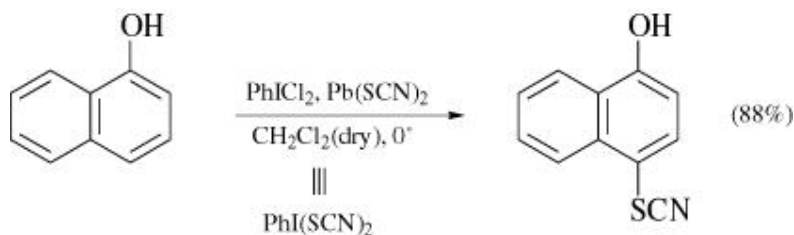
Step I. Formation of 2,4-Dinitro-6-phenyliodonium Phenolate (**73**) (118)

A solution of 2,4-dinitrophenol (1.84 g, 10 mmol) in acetonitrile (10 mL) was added to a solution of IBTA (4.3 g, 10 mmol) in acetonitrile (10 mL). After 72 hours at room temperature, **73** (1.35 g) separated from the mixture as a yellow crystalline solid, mp 195–196°; λ_{\max} (Me₂SO) 372 nm (log ϵ 4.15); IR 3086, 1585, 1560, 1555, 1260, 1090, 715 cm⁻¹; ¹H NMR [(CD₃)₂SO] δ 7.78 (m, 3 H), 8.37–8.48 (m, 2 H), 8.98 (s, 2 H); MS m/z 386 (M⁺, 93), 204 (30), 139, (95), 93 (100).

The filtrate was concentrated under reduced pressure without heating, and fresh acetonitrile (10 mL) was added. After 24 hours, a second crop of **73** (580 mg) was collected and upon repetition of the procedure the total yield of **73** amounted to 65–70%.

Step II. Formation of 5,7-Dinitro-1,3-benzoxathiole-2-thione (**113**)

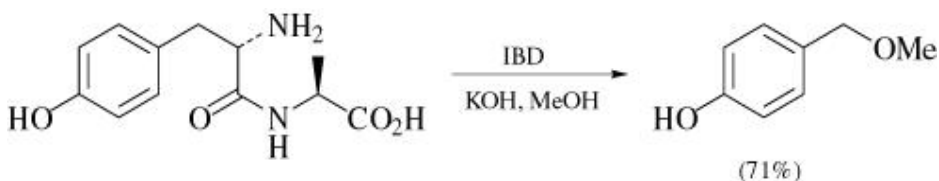
A suspension of iodonium ylide **73** (200 mg) in acetonitrile (20 mL), carbon disulfide (20 mL), and benzene (6 mL) was irradiated with a low-pressure Hg lamp (400 W, Pyrex vessel) for 9 hours with occasional shaking. Partial removal of solvents led to the precipitation of some unreacted **73** (50 mg). The filtrate was chromatographed on silica gel using hexanes-chloroform as eluant to give 73 mg (73%, based on **73** consumed) of the title product **76** as an orange crystalline solid, mp 158–159° (from chloroform-hexane); IR (Nujol) 3095, 1600, 1540 cm⁻¹; UV (EtOH) λ_{\max} 237 nm (ϵ 14, 790), 265 (12,880), 298 (14,120), 355 (10,710); ¹H NMR (CDCl₃) δ 8.44 (d, J = 2 Hz, 1 H), 8.85 (d, J = 2 Hz, 1 H); MS m/z 258 (M⁺, 45), 168 (45), 124 (48), 93 (90), 82 (85), 62 (100).



5.1.10. 4-Thiocyanato-1-naphthol [p-Thiocyanation of a Phenol] (**123**)

To an ice-cooled suspension of lead dithiocyanate (485 mg, 1.5 mmol) in dry dichloromethane (10 mL) was added (dichloriodo)benzene (330 mg, 1.2 mmol). The resulting mixture was stirred at the same temperature for 20 minutes, and then 1-naphthol (144 mg, 1.0 mmol) was added. The mixture was stirred for 1 hour, filtered, and silica gel (2 g) was added to the filtrate.

Filtration followed by concentration in vacuo gave crude product. Purification by column chromatography on silica gel using ethyl acetate-hexanes as eluant afforded 166 mg (88%) of the title product as a solid, mp 113°.

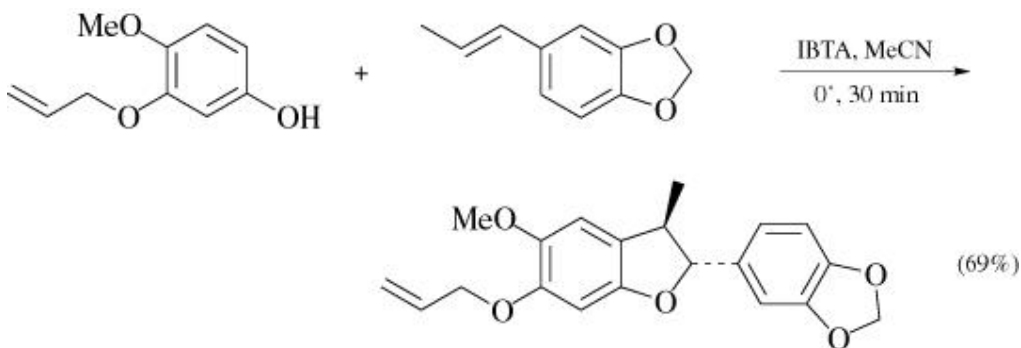


5.1.11. *p*-(Methoxymethyl)phenol [Cleavage of an Amino-Terminal Tyrosyl-Peptide Bond] (127)

Potassium hydroxide (283 mg, 5 mmol) was dissolved in methanol (50 mL) and the solution was cooled to 0°. L-Tyrosyl-L-alanine (252 mg, 1 mmol) was added to the stirred solution. IBD (322 mg, 1.0 mmol) was added over a period of 1.5 hours and stirring was continued for 1.5 hours. The reaction mixture was then acidified with acetic acid and extracted with chloroform (3 × 20 mL). The combined organic extracts were dried (MgSO₄), and concentrated in vacuo. The crude residue was purified by crystallization from etherhexane (1:1) to give 98 mg (71%) of the product, mp 76–79°; ¹H NMR (CDCl₃) δ 3.20 (s, 3 H), 4.30 (s, 2 H), 6.80–7.40 (m, 4 H).

5.1.12. (±)-*trans*-2-(3,4-Methylenedioxyphenyl)-2,3-dihydro-6-allyloxy-5-methoxy-3-methylbenzofuran [Formation of a Dihydrobenzofuran by Oxidative Cycloaddition of a Phenol to an Electron-rich Styrene] (131)

To a solution of 3-allyloxy-4-methoxyphenol (500 mg, 2.78 mmol) and (*E*)-isosafole (1.98 g, 11.1 mmol) in acetonitrile (2 mL) at 0° was added IBTA (1.43 g, 3.34 mmol). The temperature was kept at 0° for 30 minutes and the mixture was concentrated in vacuo.



Purification of the crude product by column chromatography on silica gel using ethyl acetate-petroleum ether as eluant afforded 652 mg (69%) of the title

product as a colorless crystalline solid (from ether - petroleum ether), mp 59–61°; IR (KBr) 1495, 1240, 1215, 1175, 1015 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.36 (d, $J = 6.7$ Hz, 3 H), 3.28–3.40 (m, 1 H), 3.85 (s, 3 H), 4.58 (dt, $J = 5.4, 1.5$ Hz, 2 H), 5.03 (d, $J = 8.7$ Hz, 1 H), 5.25–5.46 (m, 2 H), 5.96 (s, 2 H), 5.96–6.17 (m, 1 H), 6.51 (s, 1 H), 6.70 (d, $J = 1$ Hz, 1 H), 6.77–6.92 (m, 3 H).

6. Tabular Survey

The tables are arranged in parallel with the text and in the order of complexity of the substrates. Numbers in parentheses are yields of isolated pure products, whereas a dash indicates that no yield is reported. Where isolated yields and yields by GLC or NMR are reported, we give only the former. Where isolated yields are not reported and yields based on NMR/GLC are available, we give the latter along with a footnote. Numbers without parentheses are ratios of products.

The following abbreviations are used in the tables:

Ac	acetyl
Bn	benzyl
Boc	<i>tert</i> -butoxycarbonyl
Cbz	benzyloxycarbonyl
CSA	camphorsulfonic acid
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
HTIB	[hydroxy(tosyloxy)iodo]benzene
IBD	iodobenzene diacetate
IBTA	iodobenzene bis(trifluoroacetate)
MOM	methoxymethyl
Py	pyridine
TBAF	tetrabutylammonium fluoride
TEOC	trimethylsilylethoxycarbonyl
TFA	trifluoroacetic acid
TFE	2,2,2-trifluoroethanol
THF	tetrahydrofuran
THP	tetrahydropyranyl
Ts	<i>p</i> -toluenesulfonyl

Table IA. Formation of Quinones by Oxidation of Monophenols

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Table IB. Formation of Quinones by Oxidation of Bisphenols

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**Table II. Formation of *p*-Quinols by Oxidation of Phenols and Phenol
Tripropylsilyl Ethers**

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Table III. Formation of Quinone Acetals by Oxidation of Phenols

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Table IV. Formation of *p*-Quinol Ethers by Oxidation of Phenols

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Table V. *ipso*-Fluorination of 4-Alkylphenols

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Table VI. Formation of Spiro-Heterocyclic Compounds

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Table VII. Oxidation of *N*-Acyltyramines

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Table VIII. Formation of Hydroindolenones by Oxidative Cyclization of Phenols

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Table IX. Formation of Oxygen Heterocyclic Compounds by Oxidative Cyclization of *o*-Acylphenols

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Table X. Intramolecular Carbon-Carbon Bond Formation: Phenolic Oxidative Coupling

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Table XI. Oxidative Cyclization of *O*-Silylated Phenols to Azacarbocyclic Spirodienones

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Table XII. Formation of Iodonium Ylides and Salts

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Table XIII. *p*-Thiocyanation of Phenols

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**Table XIV. Formation of 2,3-Dimethoxy-3-Hydroxyflavanones by
Oxidation of Flavonols and Analogs**

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Table XV. Cleavage of NH₂-Terminal Tyrosyl Peptides

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**Table XVI. Synthesis of 2,3-Dihydrobenzofurans by Oxidative
Cycloadditions of Phenols to Propenylbenzenes**

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TABLE IA. FORMATION OF QUINONES BY OXIDATION OF MONOPHENOLS

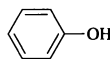
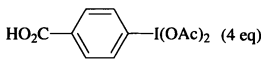
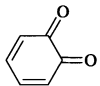
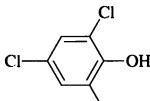
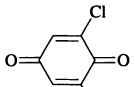
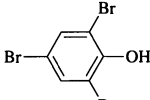
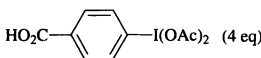
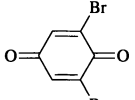
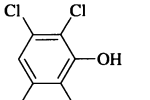
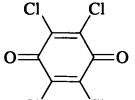
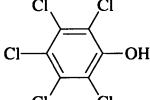
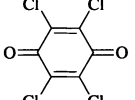
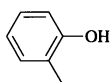
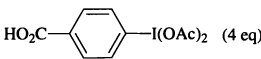
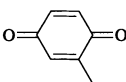
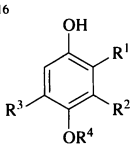
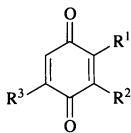
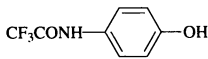
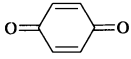
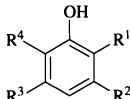
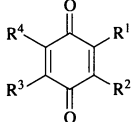
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TABLE IA. FORMATION OF QUINONES BY OXIDATION OF MONOPHENOLS (Continued)

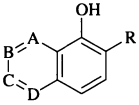
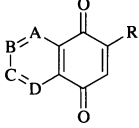
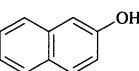
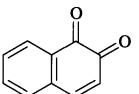
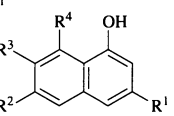
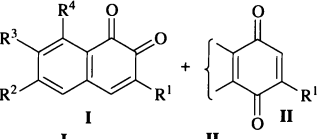
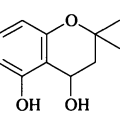
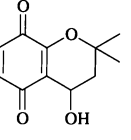
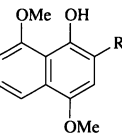
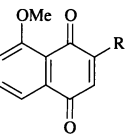
Substrate					Conditions	Product(s) and Yield(s) (%)	Refs.
R ¹	R ²	R ³	R ⁴				
Me	Me	Me	H		(PhIO) _n , BF ₃ •Et ₂ O, rt, 20 min.	(42)	156
Me	Me	Me	H		(PhIO) _n (2 eq), AcOH, 2–5 min.	(73)	156
Me	Me	Me	Me		(PhIO) _n , BF ₃ •Et ₂ O, rt, 20 min.	(58)	156
Me	Me	Me	Me		(PhIO) _n (2 eq), AcOH, 2–5 min.	(80)	156
Me	Me	Me	Me		<i>m</i> -HO ₂ CC ₆ H ₄ IO, [RuCl ₂ (PPh ₃) ₃] (1 mol%)	(43)	156
C _{9,11} 							
A	B	C	D	R			
CH	CH	CH	CH	H	IBTA (2.2 eq), H ₂ O, MeCN	(73)	58
CH	CH	CH	CH	Me	(PhIO) _n , BF ₃ •Et ₂ O, rt, 20 min.	(61)	156
CH	CH	CH	CH	Me	(PhIO) _n (2 eq), AcOH, 2–5 min.	(50)	156
CH	CH	CH	CH	Me	<i>m</i> -HO ₂ CC ₆ H ₄ IO, [RuCl ₂ (PPh ₃) ₃] (1 mol%)	(30)	156
CH	CH	CH	CH	Me	(PhIO) _n (2 eq), [RuCl ₂ (PPh ₃) ₃] (1 mol%), CH ₂ Cl ₂ , 2 min.	(18)	156
CH	CH	CH	COH	H	IBTA (2.2 eq), H ₂ O, MeCN, 0°	(58)	50,58
CH	CH	CH	COH	H	IBD (2.2 eq), H ₂ O, MeCN, 0°	(26)	50
CH	CH	CH	COH	H	(PhIO) _n , MeOH, rt	(47)	50
CH	CH	CH	COH	H	PhIO ₂ , VO ₂ acac (cat.), PhMe	(30)	50
CH	CH	CH	COH	H	C ₆ F ₅ I(O ₂ CCF ₃) ₂ , H ₂ O, MeCN	(76)	50
CH	CH	CH	COH	H	C ₆ F ₁₃ I(O ₂ CCF ₃) ₂ , H ₂ O, MeCN	(91)	50
CH	CH	CH	COMe	H	IBTA (2.2 eq), H ₂ O, MeCN, 0°	(80)	58
CH	CH	CH	N	H	IBTA (2.2 eq), H ₂ O, MeCN, 0°	(88)	58
CH	CH	N	CH	H	IBTA (2.2 eq), H ₂ O, MeCN, 0°	(80)	58
CH	CH	CMe	N	H	IBTA (2.2 eq), H ₂ O, MeCN, 0°	(82)	58
N	CMe	CMe	N	H	IBTA (2.2 eq), H ₂ O, MeCN, 0°	(70)	58
C ₁₀ 					PhIO ₂ /AcOH	 (65)	51
C ₁₀₋₁₁ 					PhIO ₂ , H ₂ O, MeCN		157
R ¹	R ²	R ³	R ⁴				
H	H	H	H			I (11)	II (63)
Me	H	H	H			(27)	(66)
H	H	Me	H			(15)	(59)
H	OMe	H	H			(18)	(62)
H	H	OMe	H			(17)	(68)
H	H	H	OMe			(16)	(46)
Me ₂ COH	H	H	H			(34)	(59)
C ₁₁ 					IBD, H ₂ O, MeCN	 (69)	59
C ₁₂ 							
R							
H					IBTA, H ₂ O, MeCN	(96-100)	49
Br					IBTA, H ₂ O, MeCN	(96-100)	49

TABLE IA. FORMATION OF QUINONES BY OXIDATION OF MONOPHENOLS (Continued)

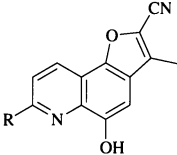
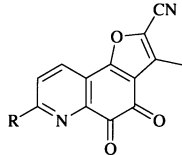
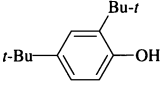
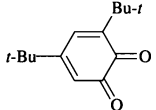
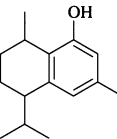
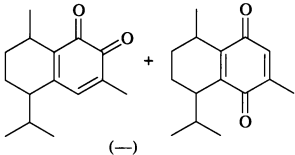
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₃₋₁₄</p> 	<p>IBTA, H₂O, MeCN, rt</p>		
<p><u>R</u></p> <p>H</p> <p>Me</p>	<p>-10°</p> <p>0°</p>	<p>(78)</p> <p>(98)</p>	<p>158</p> <p>158</p>
<p>C₁₄</p> 	<p>PhIO₂, AcOH</p>	 <p>(82)</p>	<p>51</p>
<p>C₁₅</p> 	<p>PhIO₂, H₂O, MeCN</p>	 <p>(-)</p>	<p>157</p>

TABLE IB. FORMATION OF QUINONES BY OXIDATION OF BISPHENOLS


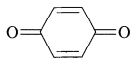
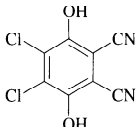
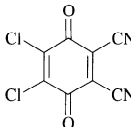
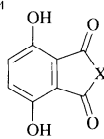
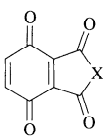
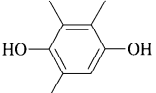
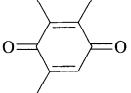
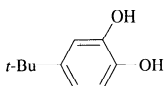
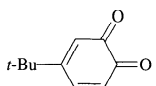
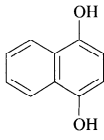
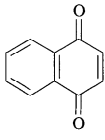
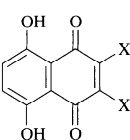
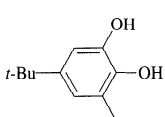
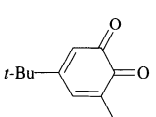
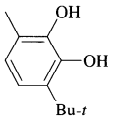
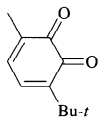
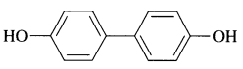
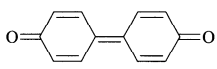
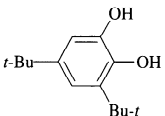
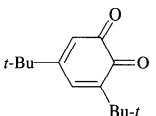
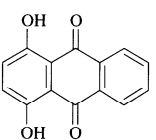
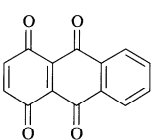
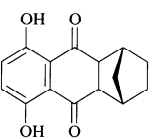
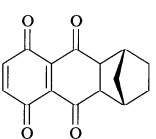
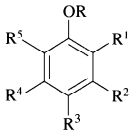
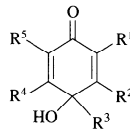
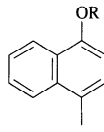
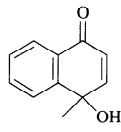
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	IBD, MeOH, rt	 (94)	52, 53
	IBTA, H ₂ O, MeCN, rt	(91)	49
	HTIB, MeCN, CH ₂ Cl ₂ , rt	(80)	52, 53
	(PhIO) _n , Et ₂ O	(70)	156
	(PhIO) _n , [RuCl ₂ (PPh ₃) ₃] (0.2 mol%), Et ₂ O	(93)	156
C ₈ 	IBTA, MeCN	 (90)	151
C ₈₋₁₄  X O NPh	IBTA, C ₆ H ₆	 (68)	57
	IBTA, CCl ₄	(97)	57
C ₉ 	IBD, MeOH, rt	 (100)	52, 53
	HTIB, MeCN, CH ₂ Cl ₂ , rt	(84)	52, 53

TABLE IB. FORMATION OF QUINONES BY OXIDATION OF BISPHENOLS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	IBD, MeOH, rt	 (99)	52, 53
	(PhIO) _n , MeCOMe	 (92)	156
	(PhIO) _n , [RuCl ₂ (PPh ₃) ₃] (1.7 mol%), MeCOMe	(85)	156
	IBTA, MeCOMe, rt, 1 h	(81)	55
X H Cl	IBTA, MeCOMe, rt, 1 h	(81)	55
C ₁₁ 	(PhIO) _n , CH ₂ Cl ₂ , rt, 1.5 h	 (70)	156
	(PhIO) _n , [RuCl ₂ (PPh ₃) ₃] (0.3 mol%), CH ₂ Cl ₂	(98)	156
	(PhIO) _n , CH ₂ Cl ₂ , rt, 1.5 h	 (48)	156
	(PhIO) _n , [RuCl ₂ (PPh ₃) ₃] (0.2 mol%), CH ₂ Cl ₂	(42)	156
C ₁₂ 	IBD, MeOH, rt	 (70)	52, 53
		(94) ^a	52, 53
C ₁₄ 	IBD, MeOH, rt	 (91)	52, 53
	(PhIO) _n , CH ₂ Cl ₂ , rt, 1.5 h	(98)	156
	(PhIO) _n , [RuCl ₂ (PPh ₃) ₃] (0.5 mol%), CH ₂ Cl ₂	(86)	156
	IBTA, MeCOMe, rt, 1 h	 (66)	55
C ₁₅ 	IBTA, MeCOMe, rt, 1 h	 (58)	56

^a This yield is based upon HPLC.

TABLE II. FORMATION OF *p*-QUINOLS BY OXIDATION OF PHENOLS AND PHENOL TRIPROPYLSILYL ETHERS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																																								
C ₇₋₁₉ 	IBTA, MeCN, H ₂ O, 0°		62																																																																																																																								
<table border="1"> <thead> <tr> <th>R</th> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td><td>H</td><td>H</td><td>H</td></tr> <tr><td>Pr₃Si</td><td>H</td><td>H</td><td>H</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>Et</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>Bn</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>H</td></tr> <tr><td>Pr₃Si</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>Me</td><td>Me</td><td>H</td><td>H</td></tr> <tr><td>Pr₃Si</td><td>H</td><td>Me</td><td>Me</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>Me</td></tr> <tr><td>Pr₃Si</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>Me</td></tr> <tr><td>H</td><td>H</td><td>Me</td><td>Me</td><td>Me</td><td>H</td></tr> <tr><td>Pr₃Si</td><td>H</td><td>Me</td><td>Me</td><td>Me</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>CH₂CO₂Me</td><td>H</td><td>H</td></tr> <tr><td>Pr₃Si</td><td>H</td><td>H</td><td>CH₂CO₂Me</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>Me</td><td>H</td><td>CO₂Et</td></tr> <tr><td>H</td><td>Br</td><td>H</td><td>Me</td><td>H</td><td>Br</td></tr> <tr><td>H</td><td>Br</td><td>H</td><td>CH₂CO₂Et</td><td>H</td><td>Br</td></tr> <tr><td>H</td><td><i>t</i>-Bu</td><td>H</td><td><i>t</i>-Bu</td><td>H</td><td><i>t</i>-Bu</td></tr> <tr><td>H</td><td><i>t</i>-Bu</td><td>H</td><td>Me</td><td>H</td><td><i>t</i>-Bu</td></tr> </tbody> </table>	R	R ¹	R ²	R ³	R ⁴	R ⁵	H	H	H	H	H	H	Pr ₃ Si	H	H	H	H	H	H	H	H	Et	H	H	H	H	H	Bn	H	H	H	Me	H	Me	H	H	Pr ₃ Si	Me	H	Me	H	H	H	H	Me	Me	H	H	Pr ₃ Si	H	Me	Me	H	H	H	Me	H	Me	H	Me	Pr ₃ Si	Me	H	Me	H	Me	H	H	Me	Me	Me	H	Pr ₃ Si	H	Me	Me	Me	H	H	H	H	CH ₂ CO ₂ Me	H	H	Pr ₃ Si	H	H	CH ₂ CO ₂ Me	H	H	H	H	H	Me	H	CO ₂ Et	H	Br	H	Me	H	Br	H	Br	H	CH ₂ CO ₂ Et	H	Br	H	<i>t</i> -Bu	H	<i>t</i> -Bu	H	<i>t</i> -Bu	H	<i>t</i> -Bu	H	Me	H	<i>t</i> -Bu		(48) (73) (48) ^a (38) ^b (60) (73) (67) (75) (67) (78) (63) (70) (27) (59) (30) (78) (67) (76) (78)	
R	R ¹	R ²	R ³	R ⁴	R ⁵																																																																																																																						
H	H	H	H	H	H																																																																																																																						
Pr ₃ Si	H	H	H	H	H																																																																																																																						
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^a 4-Acetylphenol was also obtained in 15% yield.

^b Oxidation of 4-benzylphenol gave 2-benzyl-1,4-benzoquinone as the only identifiable product (38%).

TABLE III. FORMATION OF QUINONE ACETALS BY OXIDATION OF PHENOLS

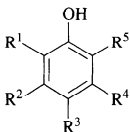
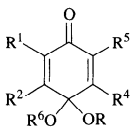
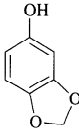
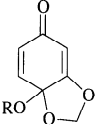
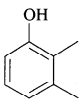
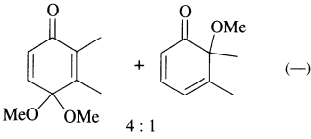
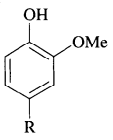
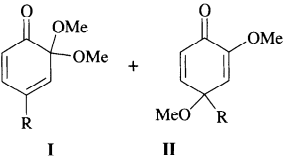
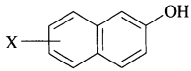
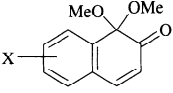
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TABLE III. FORMATION OF QUINONE ACETALS BY OXIDATION OF PHENOLS (*Continued*)

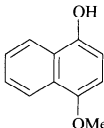
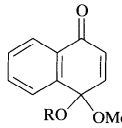
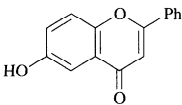
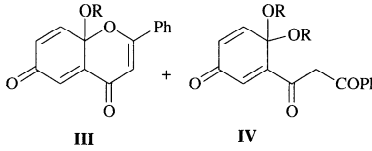
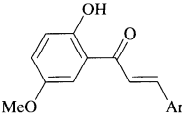
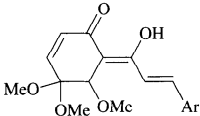
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
X			
H		(76)	71
Br		(66)	71
7-OMe		(88)	71
5-CO ₂ Me		(43)	71
6-CH(Me)CO ₂ Me		(52)	71
C ₁₁ 	IBD, ROH	 R Me (74) Et (63)	63 63
C ₁₅ 	IBD, ROH	 III IV R III IV Me (20) (31) Et (18) (34)	159 159
C ₁₆  Ar = <i>p</i> -ClC ₆ H ₄	IBTA, MeOH, 0°	 (67)	160

TABLE IV. FORMATION OF *p*-QUINOL ETHERS BY OXIDATION OF PHENOLS

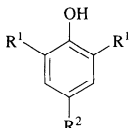
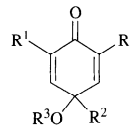
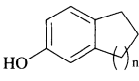
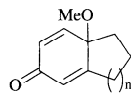
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																		
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TABLE IV. FORMATION OF *p*-QUINOL ETHERS BY OXIDATION OF PHENOLS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
C ₁₂₋₁₅																					
	IBD, MeOH																				
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>CH=CH₂</td> <td>H</td> <td>H</td> </tr> <tr> <td>CH=CH₂</td> <td>OMe</td> <td>H</td> </tr> <tr> <td>CH=CH₂</td> <td>H</td> <td>OMe</td> </tr> <tr> <td>CH=CH₂</td> <td>-[OCH₂O]-</td> <td></td> </tr> </tbody> </table>	R ¹	R ²	R ³	H	H	H	CH=CH ₂	H	H	CH=CH ₂	OMe	H	CH=CH ₂	H	OMe	CH=CH ₂	-[OCH ₂ O]-			(71) (46) (63) (34) (9)	66 66 66 66 66
R ¹	R ²	R ³																			
H	H	H																			
CH=CH ₂	H	H																			
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CH=CH ₂	-[OCH ₂ O]-																				
C ₁₈																					
			65																		
			65																		
C ₂₀																					
	IBTA, MeOH, 48 h IBTA, TFE, 1 h		106																		
C ₂₈																					
	IBTA, TFE, 24 h		107																		

^a Several other products were also formed.

TABLE V. *ipso*-FLUORINATION OF 4-ALKYLPHENOLS

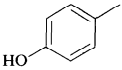
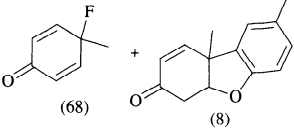
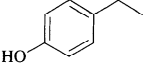
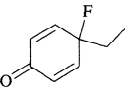
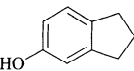
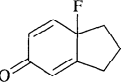
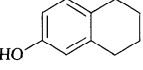
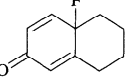
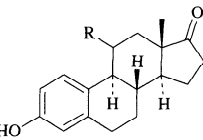
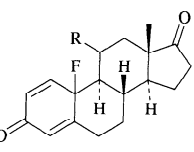
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 	Py-HF (30 : 70 w/w), IBTA	 (68) + (8)	73
C ₈ 	Py-HF (30 : 70 w/w), IBTA	 (61)	73
C ₉ 	Py-HF (30 : 70 w/w), IBTA	 (42)	73
C ₁₀ 	Py-HF (30 : 70 w/w), IBTA	 (66)	73
C ₁₈ 	Py-HF (30 : 70 w/w), IBTA	 (77) (58)	73 73
R			
H			
OH			

TABLE VI. FORMATION OF SPIRO-HETEROCYCLIC COMPOUNDS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
C ₈₋₁₄ 																																																			
<table border="1"> <thead> <tr> <th>R</th> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td></tr> <tr><td>Me</td><td>H</td><td>H</td></tr> <tr><td>Me</td><td>Br</td><td>Br</td></tr> <tr><td>OMe</td><td>OMe</td><td>H</td></tr> <tr><td>Et</td><td>H</td><td>H</td></tr> <tr><td>Et</td><td>Br</td><td>Br</td></tr> <tr><td>OEt</td><td>H</td><td>H</td></tr> <tr><td>CO₂Me</td><td>H</td><td>H</td></tr> <tr><td>CO₂Me</td><td>Br</td><td>Br</td></tr> <tr><td>CMe₃</td><td>H</td><td>H</td></tr> <tr><td>CMe₃</td><td>Br</td><td>Br</td></tr> <tr><td>C₆H₅</td><td>H</td><td>H</td></tr> <tr><td>C₆H₅</td><td>Br</td><td>Br</td></tr> <tr><td>4-BrC₆H₄</td><td>H</td><td>H</td></tr> <tr><td>4-BrC₆H₄</td><td>Br</td><td>Br</td></tr> </tbody> </table>	R	R ¹	R ²	H	H	H	Me	H	H	Me	Br	Br	OMe	OMe	H	Et	H	H	Et	Br	Br	OEt	H	H	CO ₂ Me	H	H	CO ₂ Me	Br	Br	CMe ₃	H	H	CMe ₃	Br	Br	C ₆ H ₅	H	H	C ₆ H ₅	Br	Br	4-BrC ₆ H ₄	H	H	4-BrC ₆ H ₄	Br	Br	IBTA, MeCN, reflux IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0° IBTA, MeCN, 0°	(20) (63) (58) (39) (68) (52) (68) (65) (58) (93) (89) (86) (78) (82) (77)	85 85 85 86 85 85 86 85 85 85 85 85 85 85 85 85
R	R ¹	R ²																																																	
H	H	H																																																	
Me	H	H																																																	
Me	Br	Br																																																	
OMe	OMe	H																																																	
Et	H	H																																																	
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OEt	H	H																																																	
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4-BrC ₆ H ₄	Br	Br																																																	
C ₈₋₁₆ 																																																			

TABLE VI. FORMATION OF SPIRO-HETEROCYCLIC COMPOUNDS (Continued)

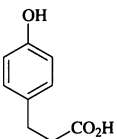
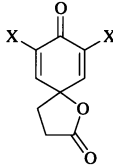
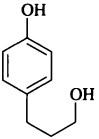
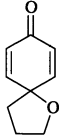
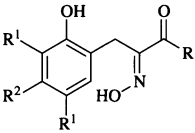
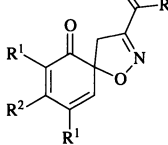
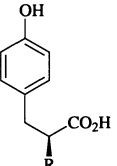
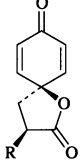
Substrate		Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y			
O	OH	IBTA, Py, MeCN, 0°-rt	(80)	84
CH ₂	OH	IBTA, Py, MeCN, 0°-rt	(86)	84
CH ₂	OH	IBTA, MeCN, 0°	(83)	76
CH ₂	OH	IBTA, Py, MeCN, 0°	(45-65)	76
CH ₂	OH	IBD, MeCN, 0°	(27)	76
CH ₂	OH	4-MeC ₆ H ₄ I(O ₂ CCF ₃) ₂ , MeCN, 0°	(69)	76
CH ₂	OH	4-MeC ₆ H ₄ I(O ₂ CCF ₃) ₂ , MeCN, Py, 0°	(35)	76
CH ₂	OH	4-ClC ₆ H ₄ I(O ₂ CCF ₃) ₂ , MeCN, 0°	(52)	76
CH ₂	OH	4-ClC ₆ H ₄ I(O ₂ CCF ₃) ₂ , MeCN, Py, 0°	(17)	76
CH ₂	OH	4-O ₂ NC ₆ H ₄ I(O ₂ CCF ₃) ₂ , MeCN, 0°	(65)	76
CH ₂	OH	4-O ₂ NC ₆ H ₄ I(O ₂ CCF ₃) ₂ , MeCN, Py, 0°	(56)	76
CH ₂	OH	1,4-[(O ₂ CCF ₃) ₂] ₂ C ₆ H ₄ , MeCN	(67)	76
CH ₂	OH	HTIB, MeCN	(53)	76
CH ₂	NHBn	IBTA, Py, MeCN, 0°-rt	(69)	84
C ₉				
		IBD (3 eq), MeCN, 0°		
			X	
			Cl (49) ^a	88
			Br (72) ^b	88
C ₁₀₋₁₄				
		IBTA, Py, MeCN, 0°-rt	 (59)	84
		IBD, MeCN, 0°		
R	R ¹	R ²		
OMe	Br	H	(46)	86
OMe	H	OMe	(40)	86
OMe	Br	OMe	(70)	86
OBu- <i>t</i>	Br	OMe	(72)	86
NH(CH ₂) ₃ OMe	H	OMe	(45)	86
NH(CH ₂) ₃ OMe	Br	OMe	(64)	86
C ₁₁₋₁₇				
		IBTA, MeCN, 0°		76
NHAc		IBTA, MeOH	(37)	76
NHAc		IBTA, MeCN, Py, 0-10°	(60-70)	78

TABLE VI. FORMATION OF SPIRO-HETEROCYCLIC COMPOUNDS (Continued)


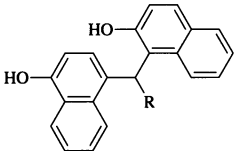
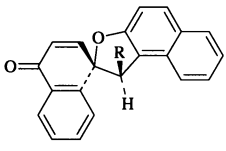
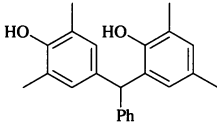
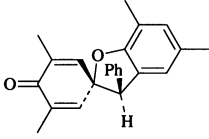
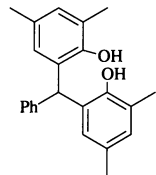
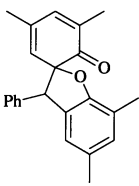
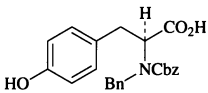
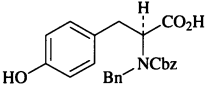
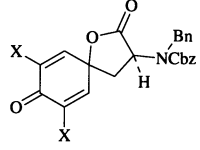
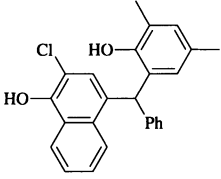
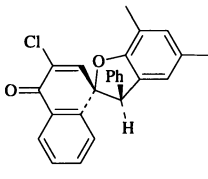
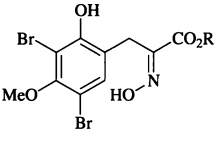
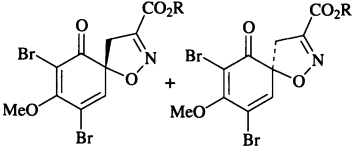
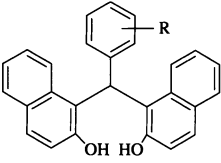
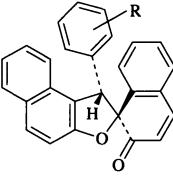
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
NHCOCF ₃	IBTA, MeCN, Py, 0–10°, 18 h	(60)	78
NHCO ₂ Bn	IBTA, MeCN, 0°	(38)	76
NHCO ₂ Bn	IBTA, MeOH	(41)	76
NHCO ₂ Bn	IBTA, MeCN, Py, 0–10°, 18 h	(60-70)	78
NHCO ₂ Bn	IBD, MeOH, 0°	(35-40)	80
NHBoc	IBTA, MeCN, 0°	(38)	76
NHBoc	IBTA, MeOH	(34)	76
NHBoc	IBTA, MeCN, Py, 0–10°, 18 h	(67)	78
NHBoc	IBD, MeOH	(68)	77
	IBTA, MeCN, Py, 0–10°, 18 h	(60-70)	78
C ₂₁₋₂₇ 	IBD, C ₆ H ₆		
R		(18) ^c	75
H		(62) ^c	75
Ph			
C ₂₃ 	IBD, C ₆ H ₆	 (34) ^c	75
	IBD, AcOH	 (43) ^{c,d}	75
C ₂₄ 	IBD (3 eq), MeCN, 0°	(32) ^e	88
	IBD (3 eq), MeCN, 0°	(41) ^f	88
	IBD (3 eq), MeCN, –5°	(43) ^{f,a}	88
	IBTA (1.1 eq), H ₂ O, MeCN, rt	(63)	88
	IBD (3 eq), MeCN, –5°		
X			
Cl		(74) ^a	88
Br		(79) ^b	88

TABLE VI. FORMATION OF SPIRO-HETEROCYCLIC COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₅ 	IBD, AcOH	 (28) ^c	75
C ₂₆  R = (-)-8-phenylmenthyl	IBD IBTA (PhIO) _n , (+)-CSA (PhIO) _n , (-)-CSA	 (31) 33% de (88) 67% de (70) 82% de (87) 82% de	86,87 86,87 86,87 86,87
C ₂₇₋₂₈ 	<u>R</u> H	 (84) ^c	74
<u>R</u> H	IBD, Py	(79) ^{c,g}	74
H	IBD, AcOH	(67) ^{c,g}	74
2-F	IBD, C ₆ H ₆	(96) ^{c,g}	74
2-F	IBD, Py	(82) ^{c,g}	74
2-F	IBD, AcOH	(56) ^{c,g}	74
3-F	IBD, C ₆ H ₆	(86) ^c	74
3-F	IBD, Py	(85) ^{c,g}	74
3-F	IBD, AcOH	(71) ^{c,g}	74
4-F	IBD, C ₆ H ₆	(87) ^c	74
4-F	IBD, Py	(80) ^{c,g}	74
4-F	IBD, AcOH	(79) ^c	74
2-OMe	IBD, C ₆ H ₆	(89) ^{c,g}	74
2-OMe	IBD, Py	(70) ^{c,g}	74
2-OMe	IBD, AcOH	(34) ^{c,g}	74
3-OMe	IBD, C ₆ H ₆	(66) ^{c,g}	74
3-OMe	IBD, Py	(81) ^{c,g}	74
3-OMe	IBD, AcOH	(76) ^{c,g}	74
4-OMe	IBD, C ₆ H ₆	(61) ^{c,g}	74
4-OMe	IBD, Py	(80) ^{c,g}	74
4-OMe	IBD, AcOH	(54) ^{c,g}	74

^a The reaction was worked up with sat. aq. NaCl.^b The reaction was worked up with sat. aq. NaBr.^c The product was obtained as a racemic mixture.^d The product was isolated as the dimer.^e The reaction was worked up with sat. aq. Na₂S₂O₃.^f The reaction was worked up with aq. 10% citric acid.^g The other diastereomer was also formed as a minor product.

TABLE VII. OXIDATION OF *N*-ACYLTYRAMINES

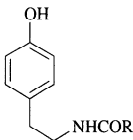
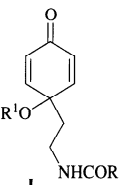
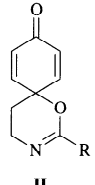
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₀₋₁₅</p>  <p>R</p>		 <p>I</p>  <p>II</p>	
Me	IBTA, MeOH	I, R = Me; R ¹ = Me (76)	67
Me	IBTA, EtOH	I, R = Me; R ¹ = Et (47)	67
Me	IBTA, <i>i</i> -PrOH	I, R = Me; R ¹ = <i>i</i> -Pr (22)	67
Me	IBTA, AcOH	I, R = Me; R ¹ = Ac (20)	67
Me	IBTA, CH ₂ Cl ₂ , K ₂ CO ₃	II, R = Me (29)	67
<i>t</i> -Bu	IBTA, MeOH	I, R = <i>t</i> -Bu; R ¹ = Me (64) + II, R = <i>t</i> -Bu (18)	67
<i>t</i> -Bu	IBTA, AcOH	I, R = <i>t</i> -Bu; R ¹ = Ac (44) + II, R = <i>t</i> -Bu (8)	67
<i>t</i> -Bu	IBTA, CF ₃ CH ₂ OH	II, R = <i>t</i> -Bu (75)	67
<i>t</i> -Bu	IBTA, CH ₂ Cl ₂ , K ₂ CO ₃	II, R = <i>t</i> -Bu (24)	67
Ph	IBTA, MeOH	I, R = Ph; R ¹ = Me (61) + II, R = Ph (27)	67
Ph	IBTA, AcOH	I, R = Ph; R ¹ = Ac (62)	67
Ph	IBTA, CF ₃ CH ₂ OH	II, R = Ph (73)	67
Ph	IBTA, CH ₂ Cl ₂ , K ₂ CO ₃	II, R = Ph (38)	67
2,6-(MeO) ₂ C ₆ H ₃	IBTA, MeOH	I, R = 2,6-(MeO) ₂ C ₆ H ₃ ; R ¹ = Me (68)	67
2,6-(MeO) ₂ C ₆ H ₃	IBTA, AcOH	I, R = 2,6-(MeO) ₂ C ₆ H ₃ ; R ¹ = Ac (57)	67
2,6-(MeO) ₂ C ₆ H ₃	IBTA, CF ₃ CH ₂ OH	II, R = 2,6-(MeO) ₂ C ₆ H ₃ (74)	67
2,6-(MeO) ₂ C ₆ H ₃	IBTA, CH ₂ Cl ₂ , K ₂ CO ₃	II, R = 2,6-(MeO) ₂ C ₆ H ₃ (17)	67

TABLE VIII. FORMATION OF HYDROINDOLENONES BY OXIDATIVE CYCLIZATION OF PHENOLS

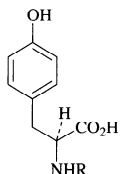
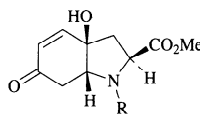

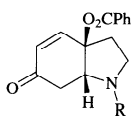
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄₋₁₇			
			
R			
Boc	IBD, MeOH, NaHCO ₃	(54)	77
Cbz	IBD, MeOH, NaHCO ₃	(54)	77
C ₁₆₋₁₇			
			
R			
Me	IBTA, CF ₃ CH ₂ OH, NaHCO ₃	(54)	67
Et	IBTA, CF ₃ CH ₂ OH, NaHCO ₃	(48)	67

TABLE IX. FORMATION OF OXYGEN HETEROCYCLIC COMPOUNDS BY OXIDATIVE CYCLIZATION OF *o*-ACYLPHENOLS

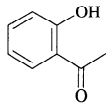
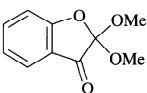
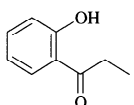
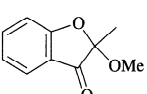
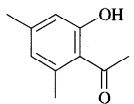
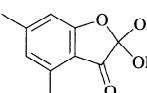
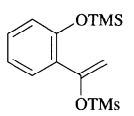
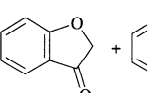
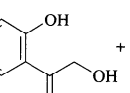
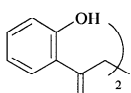
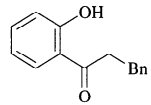
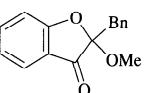
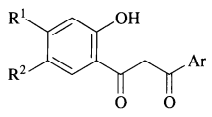
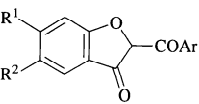
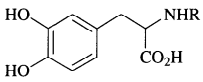
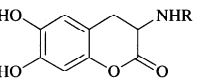
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>Coumaran-3-ones</i>			
C ₈ 	IBD, KOH, MeOH, 0–5° 1 h, rt 2 h	 (20)	89
C ₉ 	IBD, KOH, MeOH, 0–5° 1 h, rt 2 h	 (35)	89
C ₁₀ 	IBD, KOH, MeOH, 0–5° 1 h, rt 2 h	 (21)	89
C ₁₄ 	(PhIO) _n , BF ₃ ·Et ₂ O, ether, H ₂ O, –40° 1 h, –40° to rt 1 h, rt 0.5 h	 (31) +  (25) +  (5)	92
C ₁₅ 	IBD, KOH, MeOH, 0–5° 1 h, rt 2 h	 (40)	89
C ₁₅₋₁₉ 	1. IBD, KOH, MeOH, 0–5° 1 h, rt 2 h 2. HCl (6 N)		
R ¹	R ²	Ar	
H	H	Ph	(75)
H	Cl	Ph	(—)
Cl	Me	Ph	(—)
H	OMe	Ph	(—)
H	COMe	Ph	(82)
H	COMe	<i>p</i> -MeC ₆ H ₄	(80)
H	COMe	<i>p</i> -MeOC ₆ H ₄	(86)
H	COEt	<i>p</i> -MeC ₆ H ₄	(79)
H	COEt	<i>p</i> -MeOC ₆ H ₄	(82)
<i>3,4-Dihydrocoumarins</i>			
C ₁₁₋₁₇ 			
R			
Ac		IBD, AcOH	(9)
Boc		IBD, AcOH	(31)
Cbz		IBD, <i>p</i> -TsOH (cat.), AcOH	(39)

TABLE X. INTRAMOLECULAR CARBON-CARBON BOND FORMATION: PHENOLIC OXIDATIVE COUPLING

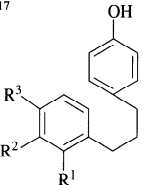
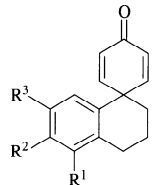
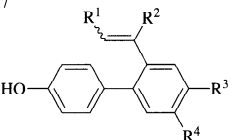
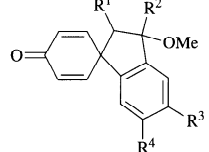
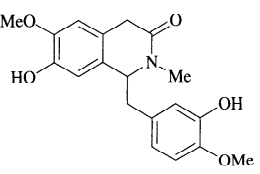
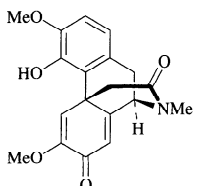
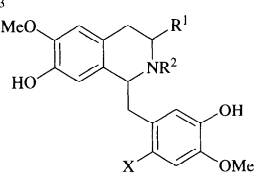
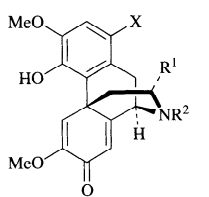
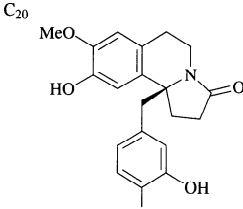
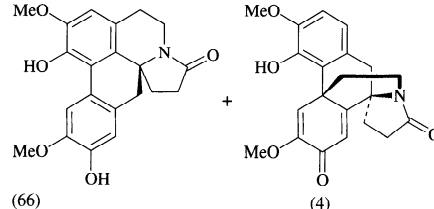
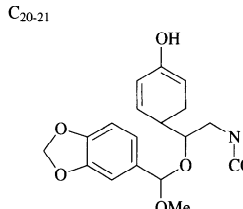
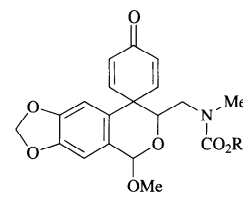
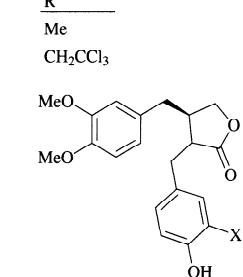
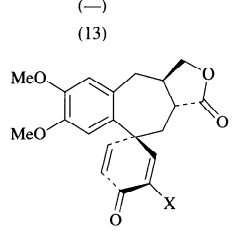
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																			
C ₁₅₋₁₇ 	IBD, MeCN, reflux, 4 h	 (30)	108																																																			
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>OMe</td></tr> <tr><td>H</td><td>OMe</td><td>H</td></tr> <tr><td>OMe</td><td>H</td><td>OMe</td></tr> <tr><td>H</td><td>OMe</td><td>OMe</td></tr> </tbody> </table>	R ¹	R ²	R ³	H	H	H	H	H	OMe	H	OMe	H	OMe	H	OMe	H	OMe	OMe																																				
R ¹	R ²	R ³																																																				
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C ₁₅₋₁₇ 	IBD, MeOH																																																					
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td><td>OMe</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>Me</td><td>OMe</td><td>H</td></tr> <tr><td>H</td><td>Me</td><td>OMe</td><td>OMe</td></tr> <tr><td>H</td><td>H</td><td>-[OCH₂O]-</td><td></td></tr> <tr><td>H</td><td>Me</td><td>-[OCH₂O]-</td><td></td></tr> <tr><td>Me</td><td>H</td><td>-[OCH₂O]-</td><td></td></tr> <tr><td>-(CH₂)₃-</td><td>H</td><td>H</td><td></td></tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	H	H	H	OMe	H	Me	H	H	H	Me	OMe	H	H	Me	OMe	OMe	H	H	-[OCH ₂ O]-		H	Me	-[OCH ₂ O]-		Me	H	-[OCH ₂ O]-		-(CH ₂) ₃ -	H	H			(56) (67) (48) (76) (34) (79) (75) ^a (50)	66 66 66 66 66 66 66 66															
R ¹	R ²	R ³	R ⁴																																																			
H	H	H	OMe																																																			
H	Me	H	H																																																			
H	Me	OMe	H																																																			
H	Me	OMe	OMe																																																			
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Me	H	-[OCH ₂ O]-																																																				
-(CH ₂) ₃ -	H	H																																																				
C ₁₉ 	IBD, CF ₃ CO ₂ H, CH ₂ Cl ₂	 (27)	98																																																			
C ₁₉₋₂₃ 																																																						
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>X</th> </tr> </thead> <tbody> <tr><td>H</td><td>CO₂Me</td><td>H</td></tr> <tr><td>H</td><td>CO₂Et</td><td>H</td></tr> <tr><td>H</td><td>CO₂Et</td><td>H</td></tr> <tr><td>H</td><td>CO₂Et</td><td>H</td></tr> <tr><td>H</td><td>CO₂Et</td><td>H</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Cl</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Br</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Br</td></tr> <tr><td>H</td><td>CO₂Et</td><td>Br</td></tr> </tbody> </table>	R ¹	R ²	X	H	CO ₂ Me	H	H	CO ₂ Et	H	H	CO ₂ Et	H	H	CO ₂ Et	H	H	CO ₂ Et	H	H	CO ₂ Et	Cl	H	CO ₂ Et	Cl	H	CO ₂ Et	Cl	H	CO ₂ Et	Cl	H	CO ₂ Et	Cl	H	CO ₂ Et	Cl	H	CO ₂ Et	Cl	H	CO ₂ Et	Cl	H	CO ₂ Et	Br	H	CO ₂ Et	Br	H	CO ₂ Et	Br	IBD, CF ₃ CO ₂ H, CH ₂ Cl ₂ IBD, AcOH, CH ₂ Cl ₂ IBTA, CF ₃ CO ₂ H, CH ₂ Cl ₂ PhI(O ₂ CCl ₃) ₂ , CCl ₃ CO ₂ H, CH ₂ Cl ₂ IBD, CF ₃ CO ₂ H, CH ₂ Cl ₂ IBD, AcOH, CH ₂ Cl ₂ IBTA, CF ₃ CO ₂ H, CH ₂ Cl ₂ PhI(O ₂ CCl ₃) ₂ , CCl ₃ CO ₂ H, CH ₂ Cl ₂ Et ₄ N ⁺ [(IOAc ₂) ₂] ⁻ , CH ₂ Cl ₂ , C ₅ H ₅ N ⁺ H ⁻ O ₂ CCF ₃ Et ₄ N ⁺ [(CO ₂ CF ₃) ₂] ⁻ , CH ₂ Cl ₂ Et ₄ N ⁺ [(CO ₂ CCl ₃) ₂] ⁻ , CH ₂ Cl ₂ IBTA, O ₂ NC ₆ H ₅ , CH ₂ Cl ₂ , -78° IBD, AcOH, CH ₂ Cl ₂ IBTA, CF ₃ CO ₂ H, CH ₂ Cl ₂ PhI(O ₂ CCl ₃) ₂ , CCl ₃ CO ₂ H, CH ₂ Cl ₂	(26) (14-32) (14-32) (14-32) (22) (14-32) (14-32) (14-32) (14-32) (—) (25-58) (25-58) (28) (14-32) (14-32) (14-32)	99 96 96 96 98 96 96 96 96 96 96 96 97 96 96 96
R ¹	R ²	X																																																				
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H	CO ₂ Et	Br																																																				

TABLE X. INTRAMOLECULAR CARBON-CARBON BOND FORMATION: PHENOLIC OXIDATIVE COUPLING (Continued)

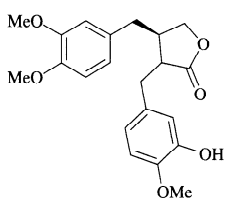
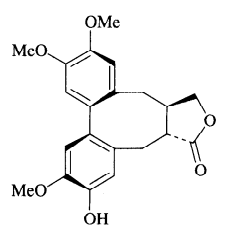
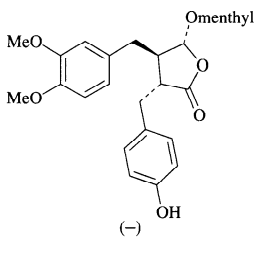
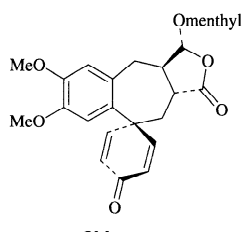
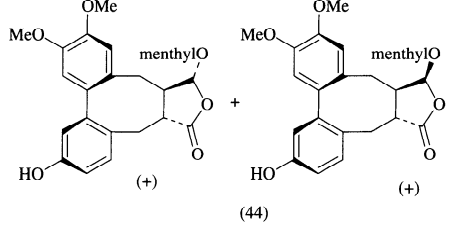
Substrate			Conditions	Product(s) and Yield(s) (%)	Refs.
R ¹	R ²	X			
H	CO ₂ Et	Br	Et ₄ N ⁺ (IOAc ₂) ⁻ , CH ₂ Cl ₂ , C ₅ H ₅ N ⁺ H ⁻ O ₂ CCF ₃	(—)	96
H	CO ₂ Et	Br	Et ₄ N ⁺ [(CO ₂ CF ₃) ₂] ⁻ , CH ₂ Cl ₂	(25-58)	96
H	CO ₂ Et	Br	Et ₄ N ⁺ [(CO ₂ CCl ₃) ₂] ⁻ , CH ₂ Cl ₂	(25-58)	96
H	CHO	H	IBD, AcOH, CH ₂ Cl ₂	(14-32)	96
H	CHO	H	IBTA, CF ₃ CO ₂ H, CH ₂ Cl ₂	(14-32)	96
H	CHO	H	PhI(O ₂ CCCl ₃) ₂ , CCl ₃ CO ₂ H, CH ₂ Cl ₂	(14-32)	96
H	CHO	Cl	IBD, AcOH, CH ₂ Cl ₂	(14-32)	96
H	CHO	Cl	IBTA, CF ₃ CO ₂ H, CH ₂ Cl ₂	(14-32)	96
H	CHO	Cl	PhI(O ₂ CCCl ₃) ₂ , CCl ₃ CO ₂ H, CH ₂ Cl ₂	(14-32)	96
H	CHO	Cl	Et ₄ N ⁺ (IOAc ₂) ⁻ , CH ₂ Cl ₂ , C ₅ H ₅ N ⁺ H ⁻ O ₂ CCF ₃	(25-58)	96
H	CHO	Cl	Et ₄ N ⁺ [(CO ₂ CF ₃) ₂] ⁻ , CH ₂ Cl ₂	(25-58)	96
H	CHO	Cl	Et ₄ N ⁺ [(CO ₂ CCl ₃) ₂] ⁻ , CH ₂ Cl ₂	(25-58)	96
H	CHO	Br	IBD, AcOH, CH ₂ Cl ₂	(14-32)	96
H	CHO	Br	IBTA, CF ₃ CO ₂ H, CH ₂ Cl ₂	(14-32)	96
H	CHO	Br	PhI(O ₂ CCCl ₃) ₂ , CCl ₃ CO ₂ H, CH ₂ Cl ₂	(14-32)	96
H	CHO	Br	Et ₄ N ⁺ (IOAc ₂) ⁻ , CH ₂ Cl ₂ , C ₅ H ₅ N ⁺ H ⁻ O ₂ CCF ₃	(25-58)	96
H	CHO	Br	Et ₄ N ⁺ [(CO ₂ CF ₃) ₂] ⁻ , CH ₂ Cl ₂	(25-58)	96
H	CHO	Br	Et ₄ N ⁺ [(CO ₂ CCl ₃) ₂] ⁻ , CH ₂ Cl ₂	(25-58)	96
H	COCF ₃	Br	IBTA, CH ₂ Cl ₂ , -40°	(21)	97
H	COCF ₃	Br	<i>o</i> -MeC ₆ H ₄ I(O ₂ CCF ₃) ₂ , CH ₂ Cl ₂ , -40°	(10)	97
H	COCF ₃	Br	<i>m</i> -MeC ₆ H ₄ I(O ₂ CCF ₃) ₂ , CH ₂ Cl ₂ , -40°	(12)	97
H	COCF ₃	Br	<i>p</i> -MeC ₆ H ₄ I(O ₂ CCF ₃) ₂ , CH ₂ Cl ₂ , -40°	(12)	97
H	COCF ₃	Br	<i>m</i> -MeOC ₆ H ₄ I(O ₂ CCF ₃) ₂ , CH ₂ Cl ₂ , -40°	(14)	97
H	COCF ₃	Br	<i>m</i> -O ₂ NC ₆ H ₄ I(O ₂ CCF ₃) ₂ , CH ₂ Cl ₂ , -40°	(8)	97
H	COCF ₃	Br	<i>p</i> -ClC ₆ H ₄ I(O ₂ CCF ₃) ₂ , CH ₂ Cl ₂ , -40°	(9)	97
H	COCF ₃	Br	(PhIO) _n , CF ₃ CO ₂ H, -40°	(11)	97
CO ₂ Me	CO ₂ Me	H	IBD, CF ₃ CO ₂ H, CH ₂ Cl ₂	(25)	99

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 <p>C₂₀</p>	<p>IBD, CF₃CO₂H, CH₂Cl₂</p>	 <p>(66)</p>	<p>(4)</p>	100
 <p>C₂₀₋₂₁</p>	<p>IBTA (2 eq), CH₂Cl₂, propylene oxide (10 eq), -10°, 0.5 h</p>	 <p>(13)</p>	<p>(—)</p>	101
<p>R</p> <p>Me</p> <p>CH₂CCl₃</p>				101
 <p>X</p> <p>H</p> <p>OMe</p>	<p>IBTA, TFE, 1 h</p> <p>IBTA, TFE, 24 h</p>	 <p>(47)</p> <p>(13)</p>		106

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TABLE X. INTRAMOLECULAR CARBON-CARBON BOND FORMATION: PHENOLIC OXIDATIVE COUPLING (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₁</p> 	IBTA, TFE, 24 h	 (40)	106
<p>C₃₀</p>  (-)	IBTA, TFE, 0.5 h	 (-) ^a	107
	IBTA, TFE, 24 h	 (+) + (+) (44)	107

^a This product was not isolated, but HPLC analysis indicated that it was the major product.

TABLE XI. OXIDATIVE CYCLIZATION OF *O*-SILYLATED PHENOLS TO AZACARBOCYCLIC SPIRODIENONES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
<p>C₁₇</p>	<p>1. TMSO-OMe 2. IBTA, TFE, rt</p>	(53)	103,104																								
<p>C₁₇₋₁₈</p>	<p>1. TMSO-OMe 2. IBTA, TFE, rt</p>	(86)																									
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>X</th> <th>Y</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>CH</td> <td>CH</td> </tr> <tr> <td>Br</td> <td>H</td> <td>CH</td> <td>CH</td> </tr> <tr> <td>H</td> <td>H</td> <td>N</td> <td>CH</td> </tr> <tr> <td>H</td> <td>H</td> <td>CH</td> <td>N</td> </tr> <tr> <td>H</td> <td>Me</td> <td>N</td> <td>N</td> </tr> </tbody> </table>	R ¹	R ²	X	Y	H	H	CH	CH	Br	H	CH	CH	H	H	N	CH	H	H	CH	N	H	Me	N	N		<p>(86) (42) (53) (64) (57)</p>	<p>102 102 103,104 103,104 103,104</p>
R ¹	R ²	X	Y																								
H	H	CH	CH																								
Br	H	CH	CH																								
H	H	N	CH																								
H	H	CH	N																								
H	Me	N	N																								

TABLE XI. OXIDATIVE CYCLIZATION OF *O*-SILYLATED PHENOLS TO AZACARBOCYCLIC SPIRODIENONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<p>C₁₈</p>	<p>1. TMSO-OMe 2. IBTA, TFE, rt</p>	(42)	103,104												
<p>C₂₀₋₂₄</p>	<p>1. TMSO-OMe 2. IBTA, TFE, rt</p>	(58)													
<table border="1"> <thead> <tr> <th>R</th> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(CH₂)₂NHCOCF₃</td> </tr> <tr> <td>H</td> <td>H</td> <td>(CH₂)₂NHTEOC</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>CH₂OAc</td> </tr> </tbody> </table>	R	R ¹	R ²	H	H	(CH ₂) ₂ NHCOCF ₃	H	H	(CH ₂) ₂ NHTEOC	Et	Me	CH ₂ OAc		<p>(58) (62) (86)</p>	<p>104 104 103,104</p>
R	R ¹	R ²													
H	H	(CH ₂) ₂ NHCOCF ₃													
H	H	(CH ₂) ₂ NHTEOC													
Et	Me	CH ₂ OAc													
<p>C₂₂</p>	<p>1. TMSO-OMe 2. IBTA, TFE, rt</p>	(71)	103,104												

TABLE XII. FORMATION OF IODONIUM YLIDES AND SALTS

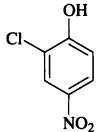
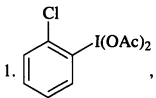
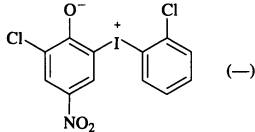
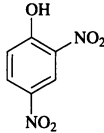
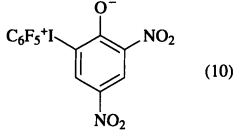
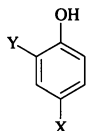
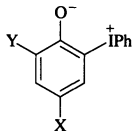
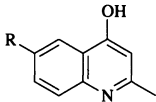
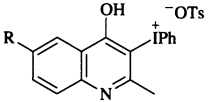
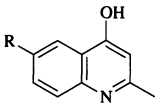
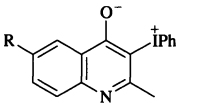
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	1.  , AcOH 2. Product dried over KOH	 (—)	111
	C ₆ F ₅ I(O ₂ CCF ₃) ₂ , MeCN	 (10)	118
C ₆₋₉ 			
<u>X</u>	<u>Y</u>		
NO ₂	H	IBD, AcOH	(84) 109
NO ₂	H	IBD, AcOH	(—) 110
NO ₂	NO ₂	IBTA, MeCN	(65-70) 118
CHO	H	IBD, AcOH	(—) 110
COMe	H	IBD, AcOH	(—) 110
CO ₂ Et	H	IBD, AcOH	(—) 110
CO ₂ Me	NO ₂	IBTA, MeCN	(30) 118

TABLE XII. FORMATION OF IODONIUM YLIDES AND SALTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
C₆₋₁₂																							
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>Br</td> </tr> <tr> <td>H</td> <td>Me</td> </tr> <tr> <td>H</td> <td>Ph</td> </tr> <tr> <td>Me</td> <td>Me</td> </tr> </tbody> </table>	R ¹	R ²	H	H	H	Br	H	Me	H	Ph	Me	Me	IBD, CH ₂ Cl ₂ IBD, CH ₂ Cl ₂ IBD, CH ₂ Cl ₂ IBD, CH ₂ Cl ₂ IBD, CH ₂ Cl ₂	(—) (—) (91) (93) (60)	121 121 121 121 121								
R ¹	R ²																						
H	H																						
H	Br																						
H	Me																						
H	Ph																						
Me	Me																						
C₈₋₁₂																							
<table border="1"> <thead> <tr> <th>R</th> <th>X</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>Br</td> </tr> <tr> <td>H</td> <td>NO₂</td> </tr> <tr> <td>H</td> <td>NO₂</td> </tr> <tr> <td>H</td> <td>COMe</td> </tr> <tr> <td>H</td> <td>COMe</td> </tr> <tr> <td>Me</td> <td>NO₂</td> </tr> <tr> <td>Me</td> <td>COEt</td> </tr> </tbody> </table>	R	X	H	H	H	H	H	Br	H	NO ₂	H	NO ₂	H	COMe	H	COMe	Me	NO ₂	Me	COEt	IBD, KOH, MeOH TsN=I ⁺ Ph, CH ₂ Cl ₂ IBD, KOH, MeOH IBD, KOH, MeOH TsN=I ⁺ Ph, CH ₂ Cl ₂ IBD, KOH, MeOH TsN=I ⁺ Ph, CH ₂ Cl ₂ IBD, KOH, MeOH IBD, KOH, MeOH	(40) (30) (35) ^a (45) (30) (40) (28) (48) (60) ^a	112,119 119 112 112,119 119 112,119 119 161 161
R	X																						
H	H																						
H	H																						
H	Br																						
H	NO ₂																						
H	NO ₂																						
H	COMe																						
H	COMe																						
Me	NO ₂																						
Me	COEt																						
C₉																							
	<p>MeOH, rt; R = H, Me, OMe</p>	<p>(60-65)</p>	122																				
C₉₋₁₅																							
<table border="1"> <thead> <tr> <th>X</th> <th>R</th> </tr> </thead> <tbody> <tr> <td>O</td> <td>H</td> </tr> <tr> <td>NH</td> <td>H</td> </tr> <tr> <td>NH</td> <td>Me</td> </tr> <tr> <td>NH</td> <td>OMe</td> </tr> <tr> <td>NMe</td> <td>H</td> </tr> <tr> <td>NPh</td> <td>H</td> </tr> </tbody> </table>	X	R	O	H	NH	H	NH	Me	NH	OMe	NMe	H	NPh	H		(93) (90) (84) (92) (93) (93)	162,163 162 162 162 162 162						
X	R																						
O	H																						
NH	H																						
NH	Me																						
NH	OMe																						
NMe	H																						
NPh	H																						
C₁₀																							
	IBD, CHCl ₃ , 0° HTIB, MeOH, rt		(92) (81)	115 164																			

TABLE XII. FORMATION OF IODONIUM YLIDES AND SALTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀₋₁₁			
 R			
H	HTIB, MeCN, CH ₂ Cl ₂	(85)	120
Cl	HTIB, MeCN, CH ₂ Cl ₂	(90)	120
Me	HTIB, MeCN, CH ₂ Cl ₂	(82)	120
OMe	HTIB, MeCN, CH ₂ Cl ₂	(80)	120
 R			
H	1. HTIB, MeCN, CH ₂ Cl ₂ 2. K ₂ CO ₃	(75)	120
Cl	1. HTIB, MeCN, CH ₂ Cl ₂ 2. K ₂ CO ₃	(83)	120
Me	1. HTIB, MeCN, CH ₂ Cl ₂ 2. K ₂ CO ₃	(73)	120
OMe	1. HTIB, MeCN, CH ₂ Cl ₂ 2. K ₂ CO ₃	(68)	120

^a The iodonium ylide was unstable, and the product was isolated as a rearranged iodoether.

TABLE XIII. *p*-THIOCYANATION OF PHENOLS

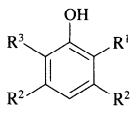
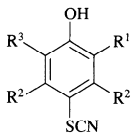
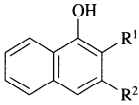
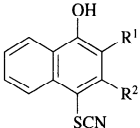
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
<p>C₆₋₁₄</p>  <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td></tr> <tr><td>CN</td><td>H</td><td>H</td></tr> <tr><td>Me</td><td>H</td><td>Me</td></tr> <tr><td><i>t</i>-Bu</td><td>H</td><td><i>t</i>-Bu</td></tr> <tr><td>Cl</td><td>H</td><td>Cl</td></tr> <tr><td>H</td><td>Me</td><td>H</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td></tr> <tr><td>CH₂=CH-CH₂</td><td>Me</td><td>Me</td></tr> <tr><td>COMe</td><td>Me</td><td>Me</td></tr> </tbody> </table>	R ¹	R ²	R ³	H	H	H	CN	H	H	Me	H	Me	<i>t</i> -Bu	H	<i>t</i> -Bu	Cl	H	Cl	H	Me	H	Me	Me	Me	CH ₂ =CH-CH ₂	Me	Me	COMe	Me	Me	PhICl ₂ , Pb(SCN) ₂ , dry CH ₂ Cl ₂ , 0°	 (93) (61) (78) (97) (64) (95) (94) (77) (78)	123
R ¹	R ²	R ³																															
H	H	H																															
CN	H	H																															
Me	H	Me																															
<i>t</i> -Bu	H	<i>t</i> -Bu																															
Cl	H	Cl																															
H	Me	H																															
Me	Me	Me																															
CH ₂ =CH-CH ₂	Me	Me																															
COMe	Me	Me																															
<p>C₁₀₋₁₆</p>  <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td></tr> <tr><td>Me</td><td>Me</td></tr> <tr><td>COMe</td><td>H</td></tr> <tr><td>CO₂Et</td><td>Me</td></tr> <tr><td>CO₂Et</td><td>CO₂Et</td></tr> <tr><td>CO₂Et</td><td>CH₂OAc</td></tr> </tbody> </table>	R ¹	R ²	H	H	Me	Me	COMe	H	CO ₂ Et	Me	CO ₂ Et	CO ₂ Et	CO ₂ Et	CH ₂ OAc	PhICl ₂ , Pb(SCN) ₂ , dry CH ₂ Cl ₂ , 0°	 (88) (67) (97) (97) (58) (88)	123																
R ¹	R ²																																
H	H																																
Me	Me																																
COMe	H																																
CO ₂ Et	Me																																
CO ₂ Et	CO ₂ Et																																
CO ₂ Et	CH ₂ OAc																																

TABLE XIII. *p*-THIOCYANATION OF PHENOLS (Continued)

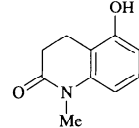
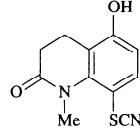
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₀</p> 	PhICl ₂ , Pb(SCN) ₂ , dry CH ₂ Cl ₂ , 0°	 (65)	123

TABLE XIV. FORMATION OF 2,3-DIMETHOXY-3-HYDROXYFLAVANONES BY OXIDATION OF FLAVONOLS AND ANALOGS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
C ₁₃₋₁₉					
Ar	R ¹	R ²			
Ph	H	H	HTIB, MeOH	(65)	124
Ph	OMe	H	HTIB, MeOH	(72)	124
Ph	H	COEt	HTIB, MeOH	(90-92)	125
Ph	H	COEt	IBD, MeOH	(90-92)	125
Ph	H	COEt	IBTA, MeOH	(92)	125
4-ClC ₆ H ₄	H	H	HTIB, MeOH	(73)	124
4-ClC ₆ H ₄	H	COEt	IBTA, MeOH	(92)	125
4-ClC ₆ H ₄	H	COEt	HTIB, MeOH	(92)	125
4-ClC ₆ H ₄	H	COEt	IBD, MeOH	(92)	125
4-MeC ₆ H ₄	H	COEt	IBTA, MeOH	(90)	125
4-MeC ₆ H ₄	H	COEt	IBD, MeOH	(90-92)	125
4-MeC ₆ H ₄	H	COEt	HTIB, MeOH	(90-92)	125
4-MeOC ₆ H ₄	H	H	HTIB, MeOH	(75)	124
4-MeOC ₆ H ₄	H	COEt	IBTA, MeOH	(90)	125
4-MeOC ₆ H ₄	H	COEt	IBD, MeOH	(90)	125
4-MeOC ₆ H ₄	OMe	H	HTIB, MeOH	(45)	124
3,4-(MeO) ₂ C ₆ H ₃	H	H	HTIB, MeOH	(77)	124
	H	COEt	IBTA, MeOH	(80)	125
	H	COEt	IBTA, MeOH	(85)	125

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TABLE XIV. FORMATION OF 2,3-DIMETHOXY-3-HYDROXYFLAVANONES BY OXIDATION OF FLAVONOLS AND ANALOGS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₉			
	HTIB, MeOH		(71) 124

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TABLE XV. CLEAVAGE OF NH₂-TERMINAL TYROSYL PEPTIDES

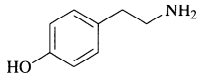
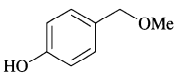
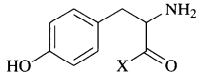
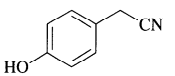
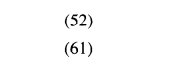
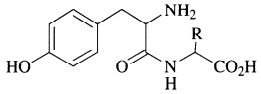
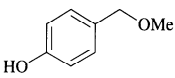
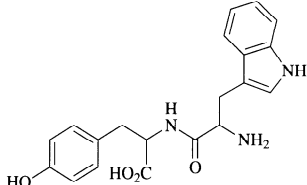
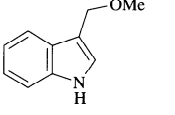
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 	IBD, KOH, MeOH, 0°	 (65)	127
C ₉ 	IBD, KOH, MeOH, 0°	 (52)  (61)	127
C ₁₁₋₁₈ 	H Me Pr- <i>i</i> CH ₂ C ₆ H ₄ OH- <i>p</i>	 (62) (71) (65) (78)	127 127 127 127
C ₂₀ 	IBD, KOH, MeOH, 0°	 (62)	126

TABLE XVI. SYNTHESIS OF 2,3-DIHYDROBENZOFURANS BY OXIDATIVE CYCLOADDITIONS OF PHENOLS TO PROPENYL BENZENES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																				
C ₇₋₁₀																																																																																							
	IBTA, MeCN		131																																																																																				
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Ar</th> <th>Molar ratio of I:II</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>1.1</td> <td>(67)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>4.0</td> <td>(71)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me^c</td> <td>1,2-(MeO)₂C₆H₃</td> <td>1.5</td> <td>(50)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>4-MeOC₆H₄</td> <td>1.0</td> <td>(57)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>H</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>1.0</td> <td>(26)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>H</td> <td>Me^c</td> <td>1,2-(MeO)₂C₆H₃</td> <td>1.5</td> <td>(23)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>H</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>3.6</td> <td>(64)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>H</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>4.0</td> <td>(34)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>1.1</td> <td>(81)</td> </tr> <tr> <td>Allyl</td> <td>H</td> <td>H</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>3.0</td> <td>(68)</td> </tr> <tr> <td>Allyl</td> <td>H</td> <td>Cl</td> <td>Me^f</td> <td>1,2-(MeO)₂C₆H₃</td> <td>4.0</td> <td>(53)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Ar	Molar ratio of I:II	Yield (%)	H	H	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	1.1	(67)	H	H	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	4.0	(71)	H	H	H	Me ^c	1,2-(MeO) ₂ C ₆ H ₃	1.5	(50)	H	H	H	H	4-MeOC ₆ H ₄	1.0	(57)	H	OMe	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	1.0	(26)	H	OMe	H	Me ^c	1,2-(MeO) ₂ C ₆ H ₃	1.5	(23)	H	OMe	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	3.6	(64)	H	OMe	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	4.0	(34)	H	Me	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	1.1	(81)	Allyl	H	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	3.0	(68)	Allyl	H	Cl	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	4.0	(53)			
R ¹	R ²	R ³	R ⁴	Ar	Molar ratio of I:II	Yield (%)																																																																																	
H	H	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	1.1	(67)																																																																																	
H	H	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	4.0	(71)																																																																																	
H	H	H	Me ^c	1,2-(MeO) ₂ C ₆ H ₃	1.5	(50)																																																																																	
H	H	H	H	4-MeOC ₆ H ₄	1.0	(57)																																																																																	
H	OMe	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	1.0	(26)																																																																																	
H	OMe	H	Me ^c	1,2-(MeO) ₂ C ₆ H ₃	1.5	(23)																																																																																	
H	OMe	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	3.6	(64)																																																																																	
H	OMe	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	4.0	(34)																																																																																	
H	Me	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	1.1	(81)																																																																																	
Allyl	H	H	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	3.0	(68)																																																																																	
Allyl	H	Cl	Me ^f	1,2-(MeO) ₂ C ₆ H ₃	4.0	(53)																																																																																	
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	IBTA, MeCN		131																																																																																				
	IBTA, MeCN		131																																																																																				

^c Denotes a *cis* isomer.

^f Denotes a *trans* isomer.

7. Acknowledgments

Thanks are due to Dr. Neena Rani, Mr. Jerry Kosmeder, Dr. Vijay Sharma, and Dr. Hitesh Batra, UIC, Chicago, and Ritu Prakash for their valuable help in the preparation of this manuscript. Financial support from the U. S. National Science Foundation through grant CHE 9520157 is gratefully acknowledged.

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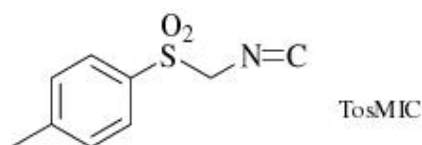
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1. Introduction

TosMIC is the acronym for 4-tolylsulfonylmethyl isocyanide or tosylmethyl isocyanide. It is the best-known member of a series of about 25 sulfonyl-substituted methyl isocyanides $\text{RSO}_2\text{CH}_2\text{NC}$ collected in Chart 1 (p. 426). TosMIC is a multipurpose synthetic reagent. It is by far the most versatile synthon derived from methyl isocyanide. (1-5) This chapter provides a complete account of the synthetic uses of TosMIC based on a literature search closed in January 1996, and supplemented with further data available to the authors. Also included are applications of some of the more important TosMIC homologs (TosCHRNC).



TosMIC is the only commercially available sulfonylmethyl isocyanide. It is a stable, colorless, practically odorless solid, which can be stored at room temperature without decomposition.

Four brief review papers on the chemistry of TosMIC have appeared, in 1980, (6) 1987, (7) 1993, (8) and 1995. (9) Several reviews on the chemistry of isocyanides in general are available. (10-25)

An effort has been made to make this chapter as complete as possible, in coverage both by tables and by references, with respect to the immediate objective: a survey of the "Synthetic Uses of TosMIC." Emphasis is on the primary products derived from reactions of TosMIC and related isocyanides, with limited reference to the further utilization of these products. Thus, the next section gives a complete account of reductive cyanation, the conversion of aldehydes or ketones into cyanides with the use of TosMIC, but for obvious reasons synthetic applications of the product cyanides are not treated in this chapter. One of the subsequent sections describes the application of TosMIC to the synthesis of pyrroles, including 2,3-divinylpyrroles, which are important precursors in a new synthesis of indoles. This latter transformation, made possible by the easy availability of the precursors through TosMIC chemistry, is afforded brief coverage.

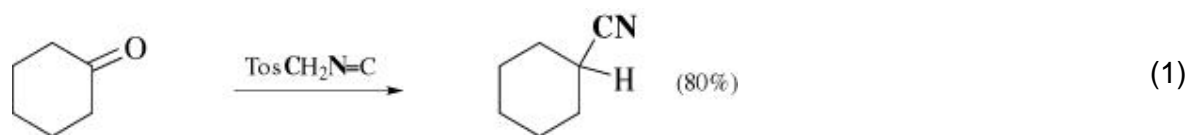
As a rule, reference to preliminary papers has been omitted when the same

information is available from the corresponding full papers. The patent literature is covered highly selectively and is cited only when providing new and relevant information. Negative results of reactions are reported in the text or tables only when at least some relevant information is available with respect to the conditions of such unsuccessful attempts.

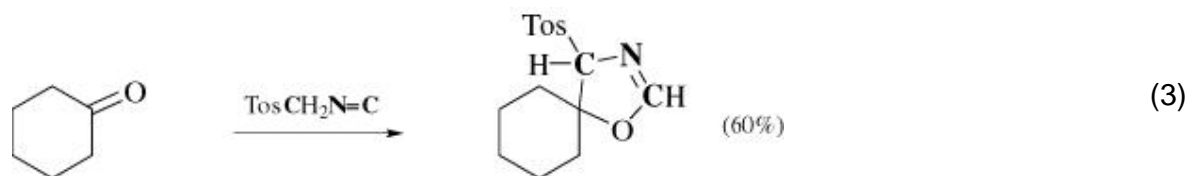
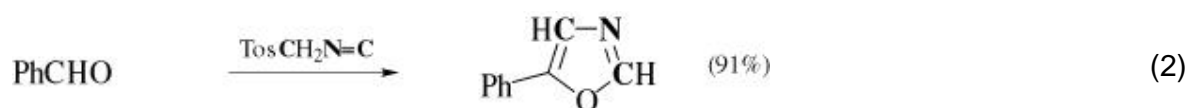
1.1. Overview of TosMIC Applications

The synthetic applications of TosMIC are diverse. Even with the same substrate molecule, TosMIC can be used to prepare quite different products simply by varying the reaction conditions. The main purpose of this overview section is to provide a quick insight into the major synthetic applications of TosMIC. Each type of reaction is illustrated by an example of wider applicability. Boldface symbols **C** and **N** are used—only in this overview section—to show which atoms of the TosMIC molecule (and TosMIC analog or homolog) end up in what positions of the final products. Where appropriate, hydrogen atoms are depicted explicitly to emphasize that the use of TosMIC leads to products in which certain positions are intrinsically unsubstituted.

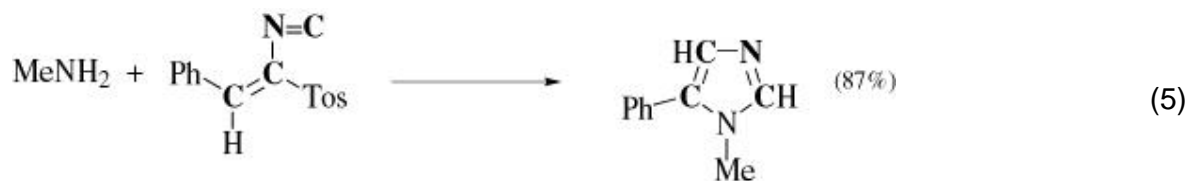
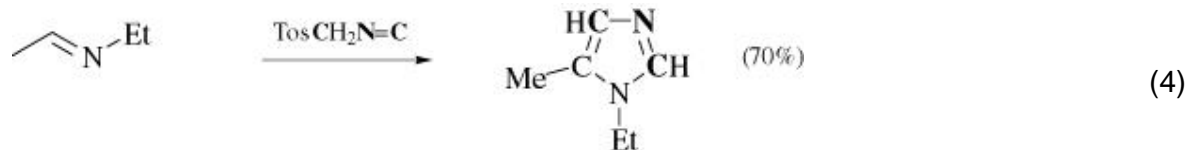
1. Reductive Cyanation of Ketones and Aldehydes (Eq. 1)



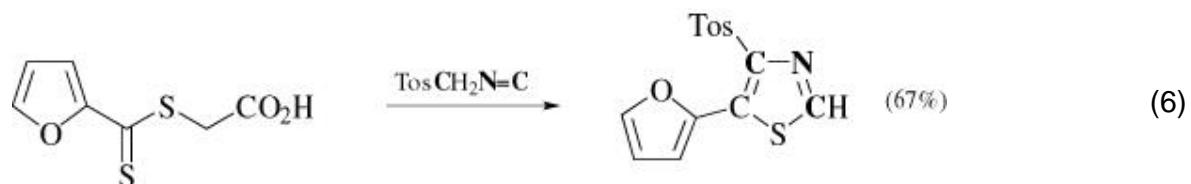
2. Synthesis of Oxazoles from Aldehydes (Eq. 2) and Oxazolines from Ketones (Eq. 3)



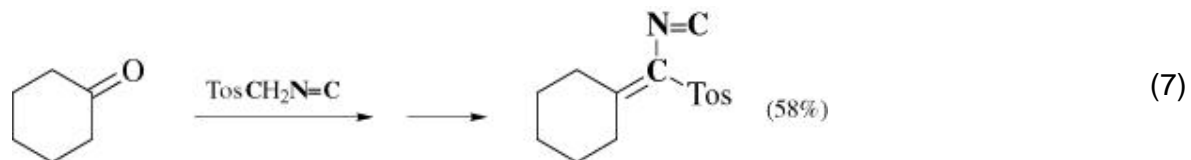
3. Synthesis of Imidazoles from TosMIC and Imines (Eq. 4) or by Using Knoevenagel-type Condensation Products of TosMIC (Eq. 5)



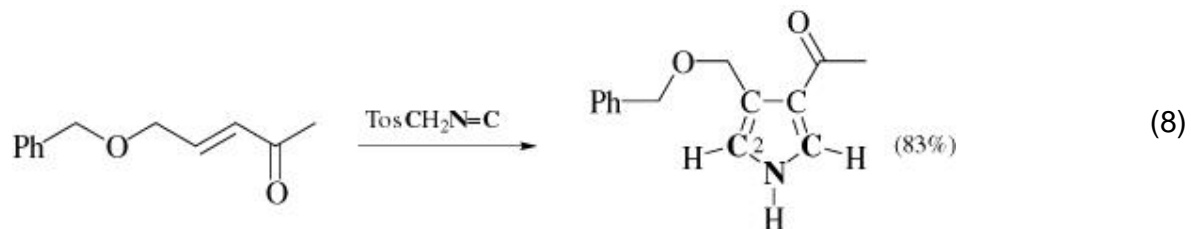
4. Synthesis of Thiazoles from Thionoesters (Eq. 6)



5. Knoevenagel-type Condensation Products from Aldehydes or Ketones (Eq. 7)

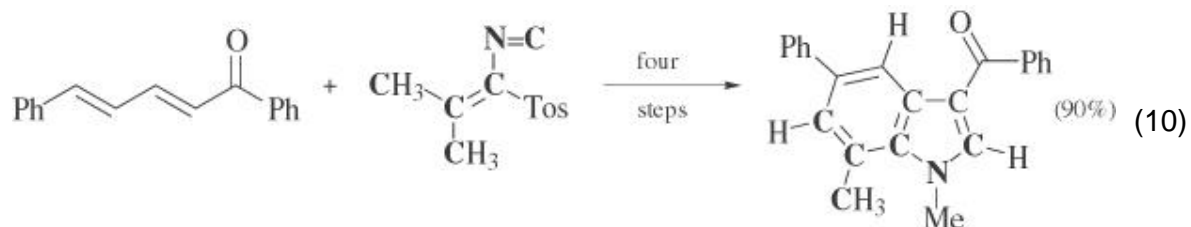


6. Synthesis of Pyrroles from TosMIC and Michael Acceptors (Eq. 8)

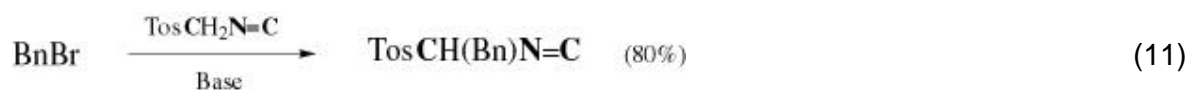




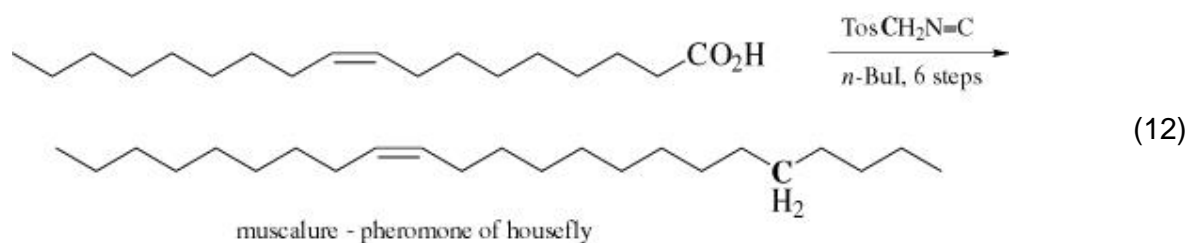
7. Synthesis of Indoles; Application of Knoevenagel-type Condensation Products of TosMIC (Eq. 10)



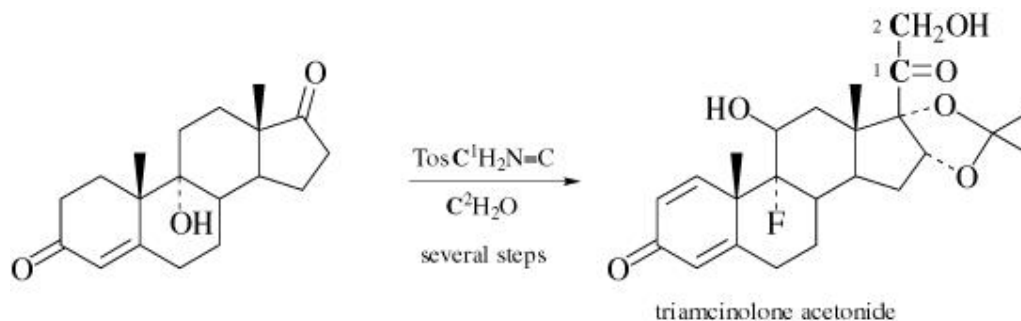
8. Phase Transfer Monoalkylation of TosMIC; Preparation of TosMIC Homologs (Eq. 11)



9. TosMIC as a Connective Reagent; Dialkylation of TosMIC (Eq. 12)



10. Synthesis of Ketones; Umpolung of Formaldehyde Reactivity (Eq. 13)



(13)

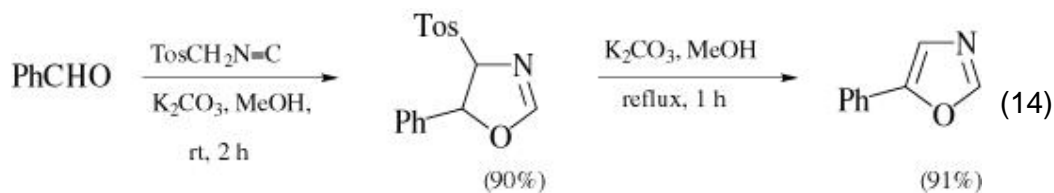
The above sequence of examples is not necessarily paralleled by the order of the following sections in which the examples are discussed in detail. The sequence of the foregoing examples emphasizes product-correspondence, such as the various azoles (Eqs. 2–6, 8–10), whereas the order of sections to follow is based primarily on mechanistic correlations.

1.2. General Aspects

The majority of the synthetic applications of TosMIC derive from the following fundamental properties:

1. TosMIC contains an activated methylene group and readily forms a stabilized, nucleophilic carbanion, which will react with a variety of electrophiles.
2. The divalent isocyano carbon usually acts as an electrophilic center, which can participate in ring closing reactions.
3. The activating tosyl group frequently operates as a moderately good leaving group in a 1,2-elimination step to produce sulfur-free products.
4. The geminal isocyano and tosyl groups in TosMIC (and in TosMIC analogs or homologs) can be looked upon as a special type of *N,S*-acetal, and in fact can be made to react accordingly.

The near quantitative formation of 5-phenyloxazole (26) from TosMIC and benzaldehyde with potassium carbonate in methanol at reflux (Eq. 14) serves to illustrate the above points 1, 2, and 3. When the reaction is carried out at room temperature, a 4-tosyloxazoline is formed; at reflux temperature subsequent base-induced elimination of 4-toluenesulfinic acid leads to 5-phenyloxazole.



Basic aspects of the chemistry of TosMIC, as exemplified by Eq. 14, are summarized in Scheme 1 (top). (7) The various reaction modes shown in this scheme may, but need not, take place in a combined fashion. For example, it is possible to alkylate the methylene group of TosMIC, once or twice, without affecting the isocyano and tosyl groups. The conversion of formaldehyde into TosMIC, and its reversal (bottom), constitutes an umpolung of the formaldehyde molecule.

1.3. Preparation of TosMIC

TosMIC was first obtained in 1967 as the unexpected result of the photolysis of tosyldiazomethane in liquid hydrogen cyanide. (27) TosMIC (CAS Registry Number 36635-61-7) is commercially available; alternatively it can be readily prepared in two steps from the commercial products sodium *p*-toluenesulfinate formaldehyde, and formamide (Eq. 16). A version of this synthesis is described in Organic Syntheses. (28) The overall yield has been further improved to 75% by modifying the conditions of the Mannich reaction. (29, 30) The procedure in the experimental section combines the best of the previous procedures into a simple preparation of TosMIC in 55% overall yield. (31)

The same approach has been used for the synthesis of labeled TosMIC compounds: Tos-¹⁴CH₂NC (CAS Registry Number 62796-16-1), (32) TosCH₂N¹³C (CAS Registry Number 60684-36-8), (33, 34) and TosCH₂¹⁵NC (CAS Registry Number 160999-37-1). (34)

A few alternative preparations of TosMIC are known. Two of these are worth mentioning here because they have been used in the synthesis of TosMIC analogs RSO₂CH₂NC: the reaction of 4-toluenesulfonyl fluoride with lithiummethyl isocyanide; (34-37) and the oxidation of 4-CH₃C₆H₄SCH₂NHCHO, followed by dehydration. (35, 38-40) Alternatives to the latter dehydration using phosphorus oxychloride and triethylamine have been reported. (41, 42)

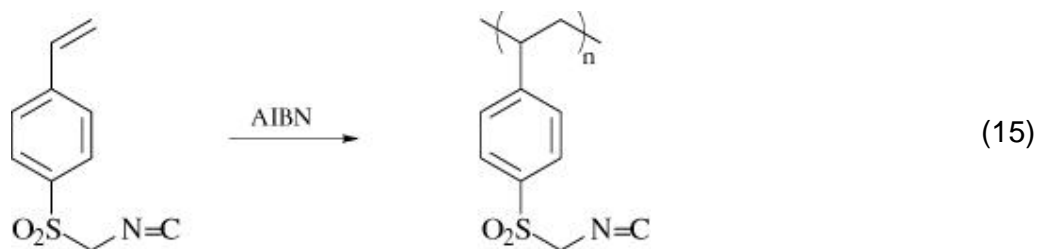
1.4. Analogs of TosMIC

Chart 1 depicts the TosMIC analogs RSO₂CH₂NC with R other than 4-tolyl. By and large these compounds show the same chemistry as TosMIC, but they have been used much less frequently for synthetic purposes than TosMIC

proper. In general, the crystalline compounds are more stable to storage. The chemistry of the TosMIC analogs of Chart 1 is not covered exhaustively in this chapter. One analog, however, is worth mention:

(-)-*S*-phenyl-*N*-tosylsulfonimidomethyl isocyanide (**8**), is a chiral TosMIC analog that bears its stereogenic center close to the prime reaction site, the methylene group. (40, 43)

Polymeric TosMIC analogs have been prepared in high yields by free-radical polymerization of (4-ethenylphenyl)sulfonylmethyl isocyanide (Eq. 15). (44) The polymeric TosMIC analogs have been used for the reductive cyanation of ketones and for the synthesis of imidazoles.

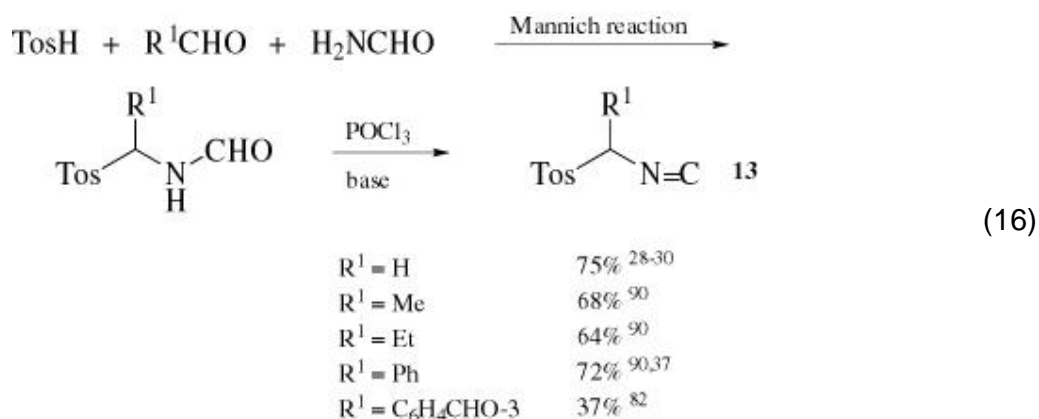


The eliminated (polymeric) sulfinic acids can be reused. (44) Further aspects of the chemistry of TosMIC analogs are discussed at the end of this chapter.

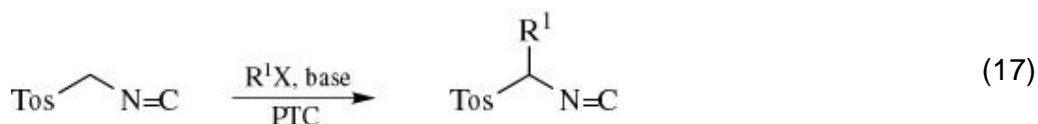
1.5. Homologs of TosMIC

Most synthetic applications of TosMIC are based on an initial reaction of TosMIC anion (TosC^-HNC). Obviously, related anions may be derived from monosubstituted TosMIC derivatives TosCHR^1NC **13**. Such homologs **13** can be used synthetically in most of the synthetic transformations of TosMIC except those requiring both acidic hydrogens, notably reductive cyanation (Eq. 1) and the Knoevenagel-type condensation reaction (Eq. 7).

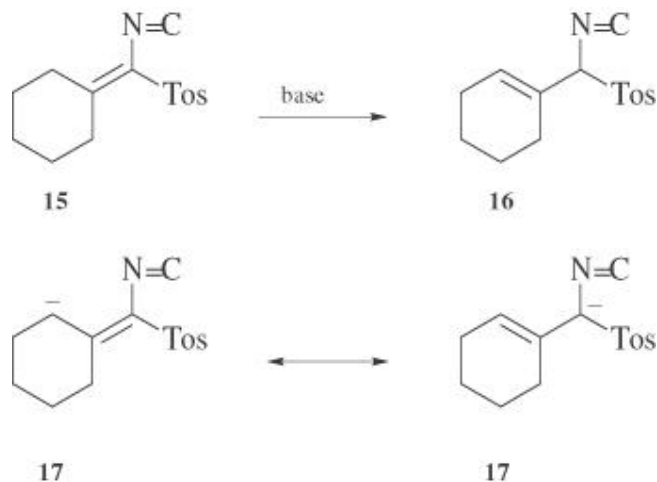
Since disubstituted TosMIC derivatives $\text{TosCR}^1\text{R}^2\text{NC}$ **14** cannot form carbanions, these compounds are treated as TosMIC-derived products. They are crucial intermediates in the TosMIC-based synthesis of ketones (Eq. 13) and in the connective reagent application (Eq. 12). Several compounds TosCHR^1NC **13** have been prepared by a Mannich reaction followed by dehydration (Eq. 16).



Most of the alkyl-substituted compounds **13** ($\text{R}^1 = \text{alkyl}$) are prepared by phase transfer catalyzed (PTC) monoalkylation of TosMIC (Eq. 17, Table VI). This is the method of choice, since TosMIC is commercially available. Aryl derivatives ($\text{R}^1 = \text{aryl}$) are accessible via the Mannich reaction (Eq. 16), or by reaction of arenesulfonyl fluorides with lithiobenzyl isocyanides. (37)



The (formal) Knoevenagel condensation products of ketones and aldehydes with TosMIC (Eq. 7) deserve special attention. When a γ carbon in these condensation products bears a hydrogen, as for example in cyclohexanone derivative **15**, the tautomeric hydrogen shift to **16** provides a TosMIC derivative with an alkenyl substituent (Eq. 18).



(18)

In most reactions, the β , γ -unsaturated compounds are the thermodynamically more stable tautomers. The α , β -unsaturated condensation product of TosMIC and acetone is one of the few established exceptions to this rule. Reactions of anion **17** obtained by deprotonating either **15** or **16** and related compounds further extends the chemistry of TosMIC derivatives.

Intermediates of type **17** play a crucial role in reactions such as Eqs. **10** and **13**. Since Knoevenagel condensation products such as **15** and **16** find other applications as well, they are considered primarily to be the products of TosMIC reactions. The sodium borohydride reduction of the α , β double bond of compounds **15** provides another entry into monosubstituted TosMIC derivatives **13**. (45)

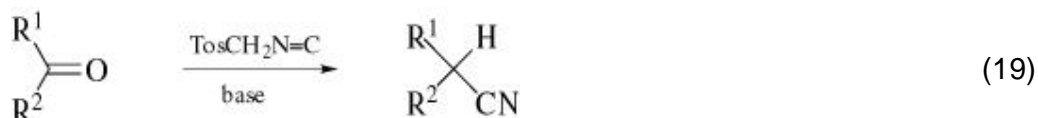
A related series of synthons exists that can act as TosMIC equivalents: tosylmethyl substituted carbodiimides ($\text{TosCH}_2\text{N}=\text{C}=\text{NR}$), (46) imidates and thioimidates [$\text{TosCH}_2\text{N}=\text{C}(\text{XCH}_3)\text{R}$; X = O, S], (47-51) and imino(dithio)carbonates [$\text{TosCH}_2\text{N}=\text{C}(\text{XR})_2$; X = O, S]. (47, 51) These synthons have been used occasionally for the synthesis of azoles with a substituent at position 2. (52)

The following sections are arranged according to the various types of products that have been realized with the use of TosMIC, since structurally different products may be derived from the same substrate molecule, simply by varying the reaction conditions.

2. Reductive Cyanation; One-Carbon Homologation of Ketones and Aldehydes

2.1. Ketones

Ketones are converted in good yields to cyanides upon reaction with TosMIC and base in nonprotic solvents (Eq. 19). (32, 53, 54)



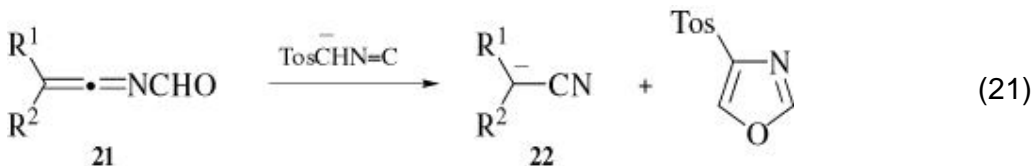
The reductive cyanation of ketones is carried out in one operation, although the reaction involves several stages. The reaction of adamantanone with ^{14}C -labeled TosMIC shows that the cyano carbon of the product is derived from the TosMIC methylene group (Eq. 20). (32)



The vertical track of Scheme 2 shows the probable mechanism of the reductive cyanation reaction. (32, 55) Nucleophilic attack of TosMIC anion at the ketone carbonyl leads to oxazoline anion **18**. In nonprotic solvents a hydrogen shift to **19** is followed by electrocyclic ring opening to **20**, which at or above room temperature loses 4-toluenesulfinate anion to afford *N*-formylketenimine **21** (which has not been isolated). The formyl group of **21** is lost upon subsequent attack of a nucleophile (for example alkoxide) to give anion **22**. Workup with water provides cyanide **23**, obtained as an equilibrium mixture of diastereomers when ketones with stereogenic centers are used.

Occasionally, TosMIC anion has been found to act as the nucleophile in the deformylation of **21** to **22**, resulting in the formation of 4-tosyloxazole (Eq. 21). (32, 56) Since this reaction causes an undesirable consumption of a second

equivalent of TosMIC, the reductive cyanation is best carried out in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) containing 1 to 2 equivalents of methanol or ethanol, producing a formate ester, rather than 4-tosyloxazole. (32, 56)



The presence of small amounts of alcohol in the otherwise nonprotic solvents does not significantly promote the undesirable reactions $18 \rightarrow 24$ and $20 \rightarrow 25$, and reductive cyanation proceeds efficiently.

Two aspects of Scheme 2 are important in relation to later sections of this chapter:

1. Reductive cyanation of ketones and aldehydes is the end point of a series of sequential reactions ultimately leading to cyanides (Eqs. 20 and 21).
2. By changing the reaction conditions, quite different products may be formed even from the same starting materials.

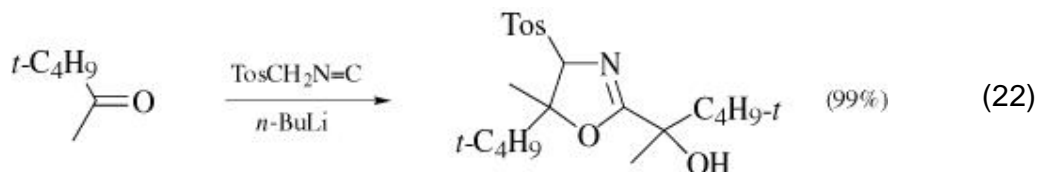
At this stage of the discussion it is necessary only to realize that under protic conditions intermediates 18 or 20 may be sidetracked into compounds 24 and 25, respectively. Both 4-tosyloxazolines 24 and unsaturated tosylformamides 25 are important products for further synthetic applications, as will be shown later.

Reductive cyanation has been applied to many different ketones. The reaction fails when the carbonyl carbon is severely sterically screened from nucleophilic attack by TosMIC anion, as exemplified by di-*tert*-butyl ketone, which is recovered unchanged even under forcing conditions (170 hours at 45°), (32) and when the ketone is easily deprotonated, exemplified by benzyl phenyl ketone.

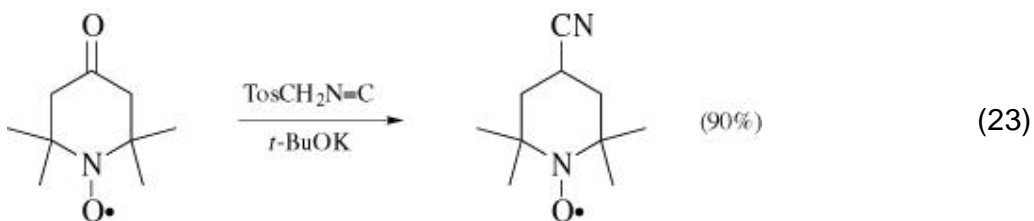
The reductive cyanation of ketones is usually carried out in DME with 1.1 equivalents of TosMIC and 2 equivalents or more of potassium *tert*-butoxide. Reaction temperatures and reaction times strongly depend on the reactivity of the ketone, and range from 0 to 50° and 1 to 72 hours, respectively. (32) Occasionally, THF, dimethyl sulfoxide (DMSO), and hexamethylphosphoramide (HMPA) have been used as solvents or cosolvents. Most probably, all reactions carried out in DME could be carried out equally well in the cheaper THF. (55) An excess of base is used to suppress

cyclodimerization reactions of TosMIC, which are initiated by the addition of TosMIC anion to the isocyano carbon of TosMIC. (32, 37, 56)

In a few cases potassium *tert*-butoxide may be replaced by sodium ethoxide. *n*-Butyllithium cannot be used in reductive cyanation reactions, although this base is quite useful in other applications of TosMIC; the proton shift in 2-lithiooxazoline **18** to isomer **19** (Scheme 2, M = Li) apparently is retarded such that isomer **18** will react with a second molecule of ketone (Eq. 22). (55)



Selective reductive cyanation of ketones is possible in the presence of other functional groups that do not normally react with TosMIC: ethers, thioethers, acetals, aromatic halides, aliphatic hydroxy groups, esters, lactones, urethanes, aromatic nitro groups, and isolated C – C multiple bonds survive. Reductive cyanation has been successfully applied to a stable radical species (Eq. 23). (57)



The one-step reductive cyanation of ketones with the use of TosMIC is much more convenient (especially as far as handling of reagents is concerned) than a three-step approach that was developed almost simultaneously. (58) The latter process, detailed in *Organic Syntheses* for the conversion of cyclohexanone to cyclohexyl cyanide, (59) makes use of methyl hydrazine carboxylate, hydrogen cyanide, and bromine. A more recent, interesting alternative involves the samarium (II) iodide reduction of α -cyanophosphates, formed in situ from ketones (or aldehydes) by reaction with diethyl cyanophosphate and lithium cyanide. (60, 61)

2.2. Aldehydes

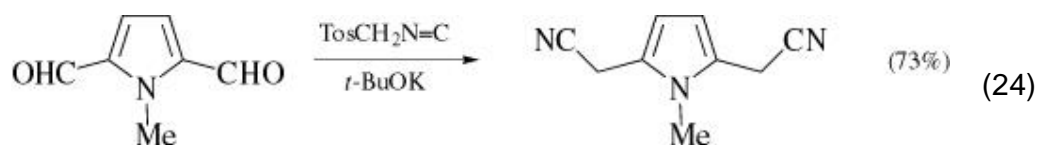
Reductive cyanation is also applicable to aldehydes, although it is less frequently employed (Scheme 2, $R^1 = H$). A slight modification of reaction conditions is needed to obtain good results (see below). When the reductive cyanation of aldehydes is carried out under conditions typically employed for ketones, yields are low. Benzaldehyde, for example, gives benzyl cyanide in only 15% yield. (62) Byproducts to be expected are oxazoles and/or oxazolines. As noted earlier, a crucial step in reductive cyanation is electrocyclic ring opening of **19** to **20** (Scheme 2), which requires a proton shift from **18** to **19**. With aldehydes, a competing proton shift becomes possible from **18a** (i.e. **18** where $R^1 = H$) to **26**, which initiates the elimination of Tos^- to give oxazoles **27** (Scheme 3).

In protic solvents the formation of oxazoles **27** is well established in the reaction of TosMIC with aromatic aldehydes (Scheme 3). The acidity of the hydrogen at C5 in anion **18a**, when R^2 is aromatic, is such that the hydrogen shift **18a** \rightarrow **26** can compete with the proton shift **18a** \rightarrow **19a**. When the C5 hydrogen is less acidic, as is the case for aliphatic aldehydes, oxazoles are not formed. (63) In methanol at reflux, the tosyl group in oxazoline **24** (Scheme 2) is replaced by MeO (Eqs. 30 and 32).

In actual practice the problem of side reactions in the reductive cyanation of aldehydes is largely overcome by carrying out the reaction in two operations (see [Experimental Procedures](#)). First, the aldehyde is allowed to react with TosMIC anion at low temperatures (-50 to -20°) under nonprotic conditions to carry the reaction all the way to intermediate **20** (Scheme 2, $R^1 = H$). The reaction is then completed by heating, after addition of excess methanol. (62, 64) Whether this two-step procedure is beneficial to the lower yielding reductive cyanations of ketones remains to be seen.

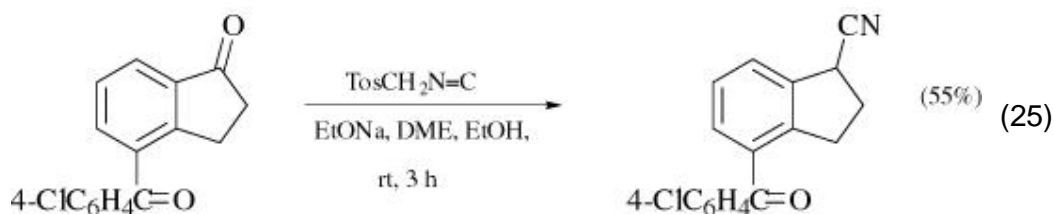
2.3. Dicarbonyl Compounds; Less Reactive Ketones

A double reductive cyanation has been carried out with symmetrical dialdehydes (Eq. 24). (65)



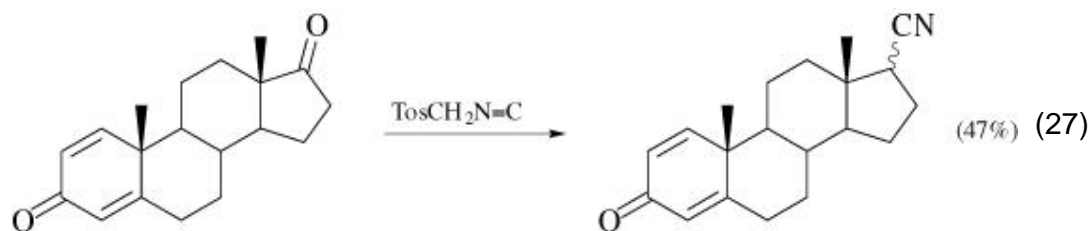
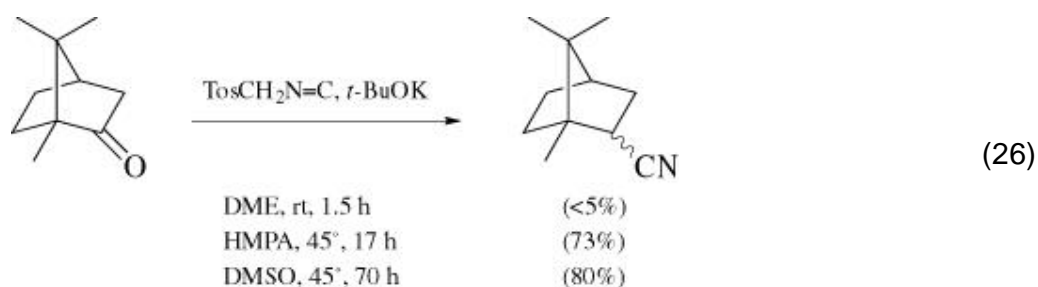
It is not known whether a single reductive cyanation of just one of the aldehyde functions of the same substrate is possible in an efficient manner. However,

several reductive monocyanations of diones have been described albeit only for unsymmetrical starting materials (Eq. 25). (66)



Reductive cyanations of less reactive ketones such as benzophenone and hindered ketones such as camphor require longer reaction times (Eq. 26). (32)

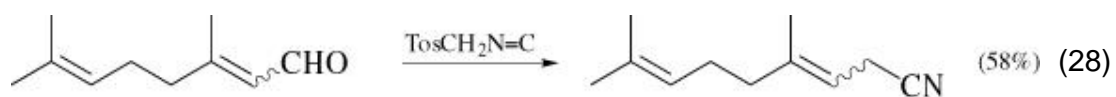
Monocyanation of 1,4-cyclohexanedione has been described only for the monoketal derivative. (67) The reactivity of the keto groups at C3 and C17 in steroids with two double bonds in the A ring is sufficiently different to allow a selective reductive cyanation at C17 (Eq. 27). (32) However, without the 1,2 double bond of the A ring, protection of the C3 keto group becomes necessary. The less reactive steroidal C11 carbonyl does not need protection, as demonstrated by the selective cyanation of 3,3-(ethylenedioxy)androst-5-ene-11,17-dione. (56)



2.4. α , β -Unsaturated Aldehydes

Although α , β -unsaturated ketones undergo conjugate addition of TosMIC anion to give pyrroles (Eq. 8), the higher electrophilicity of the aldehyde carbon

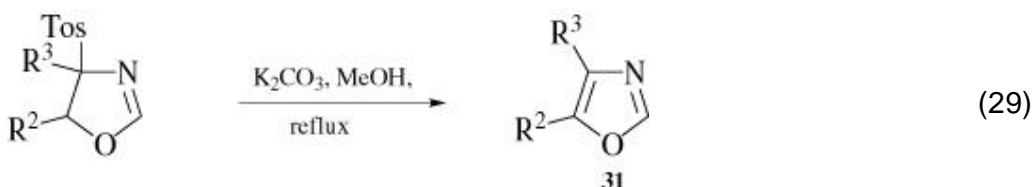
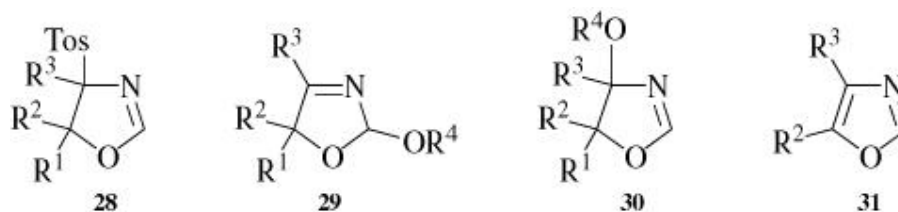
permits reductive cyanation of α , β -unsaturated aldehydes, as exemplified by the reductive cyanation of citral (Eq. 28). (62)



In closing this section, it may be noted that an efficient reversal of Eq. 19, an oxidative decyanation, has been reported for methyl cyanides with at least one aryl substituent in the form of a phase transfer catalyzed reaction with oxygen. (68)

3. Synthesis of Oxazolines and Oxazoles from Carbonyl Compounds

Base-promoted reactions of TosMIC with ketones or aldehydes in alcoholic solvents provide five-membered heterocycles containing nitrogen and oxygen. Three different types of heterocycles may be formed in alcoholic solution from TosMIC and ketones: 4-tosyl-2-oxazolines **28**, 2-alkoxy-3-oxazolines **29**, and 4-alkoxy-2-oxazolines **30** ($R^3 = H$). The same type of heterocycles **28**, **29**, and **30** ($R^1 = R^3 = H$) result from reacting TosMIC with aldehydes, but in this case the formation of oxazoles **31** is also possible (Eq. 29).

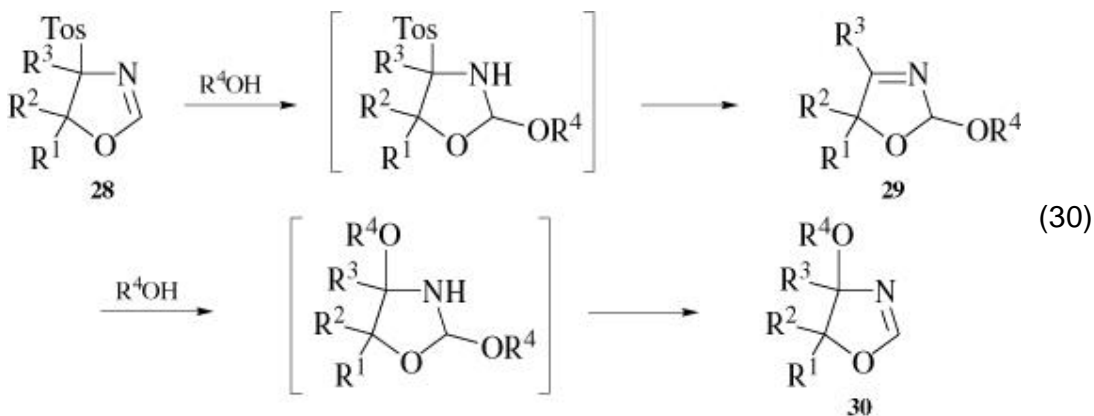


4-Tosyloxazolines **28** are the initial products in all of these reactions, and are formed simply by stirring TosMIC and the carbonyl compound with a catalytic amount of base in methanol or ethanol at room temperature. At elevated temperatures and/or prolonged reaction times in alcohol, tosyloxazolines **28** are converted to one of the compounds **29** to **31**. Which of these is formed depends on the nature of the substituents R^1 , R^2 , and R^3 .

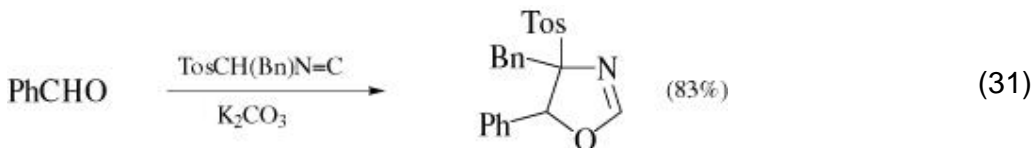
3.1. Oxazolines and Products Derived Therefrom

Elimination of 4-toluenesulfinic acid is obviously not possible with tosyloxazolines **28** derived from ketones. Instead, the tosyl group may be replaced by an alkoxy group to give 2-alkoxyoxazolines **29** or 4-alkoxyoxazolines **30** by reaction with the alcoholic solvent. These reactions

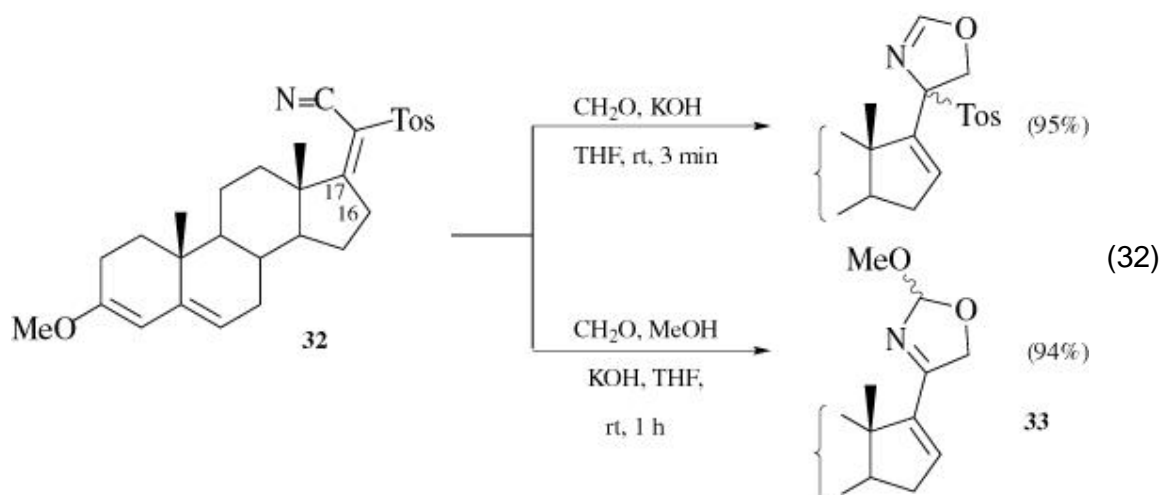
are assumed to take place in a combined addition-elimination process to give **29**, or by two such processes to give isomer **30** (Eq. 30).



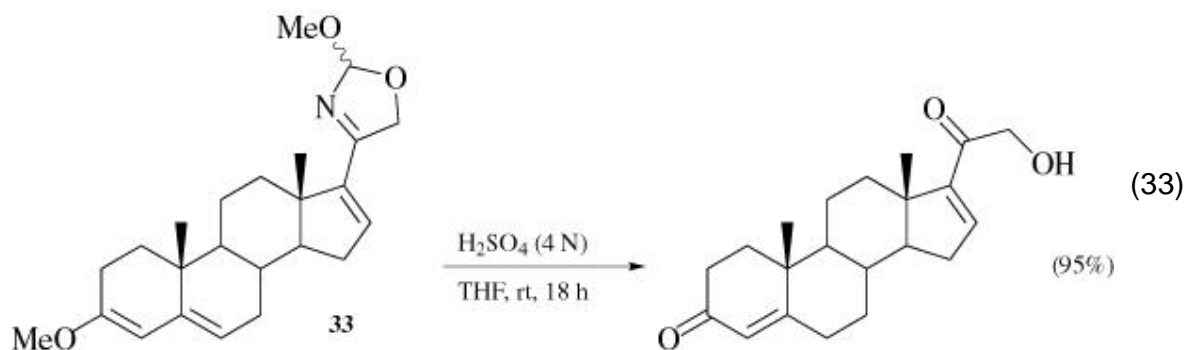
On the basis of available information, 4-alkoxy-2-oxazolines **30** appear to be the main (or sole) products when $R^3 = H$, whereas 2-alkoxy-3-oxazolines **29** are formed exclusively when $R^3 = \text{alkyl}$. Whereas the reductive cyanation of ketones or aldehydes requires that the methylene group of TosMIC be unsubstituted, this is no longer a necessary condition for the synthesis of oxazolines **28**, **29**, and **30** and oxazoles **31**. Monosubstituted TosMIC homologs give the same series of products **28** to **31** with $R^3 = H$. For example, the reaction of 2-phenyl-1-tosylethyl isocyanide gives a 4-tosyloxazoline of type **28** (Eq. 31). (69)



The next example, Eq. 32, amounts to conversion of a 17-oxosteroid to a 2-methoxyoxazoline of type **29** using TosMIC, formaldehyde, and methanol. (70) First, 3-methoxyandrosta-3,5-dien-17-one is converted to **32**, the formal Knoevenagel condensation product of TosMIC and the 17-oxosteroid. Condensation products of type **32** can be used effectively as monosubstituted TosMIC homologs through γ deprotonation, as discussed earlier. Thus, a 4-tosyloxazoline **28** is formed in the reaction of steroid **32** with formaldehyde (Eq. 32).



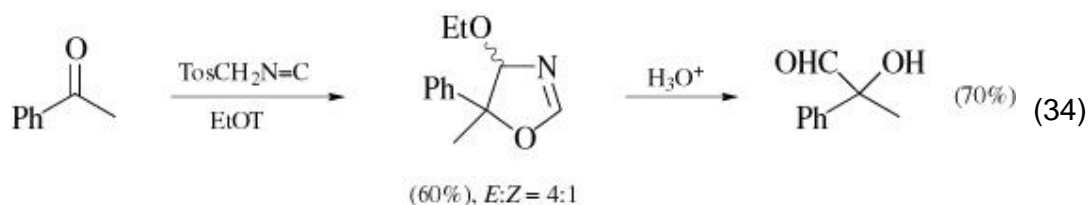
When the reaction of **32** with formaldehyde is carried out in the presence of 5 equivalents of methanol, the initially formed 4-tosyloxazoline is converted in situ into 2-methoxyoxazoline **33** (Eq. 32) by an addition-elimination process as described in Eq. 30.



The synthetic utility of oxazolines **28–30**, in addition to being intermediates in the synthesis of oxazoles when $R^1 = H$, relies above all on their propensity to hydrolysis. Thus, acid hydrolysis of 2-methoxyoxazoline **33** leads to a 17-(hydroxyacetyl)steroid in high yield (Eq. 33). (70)

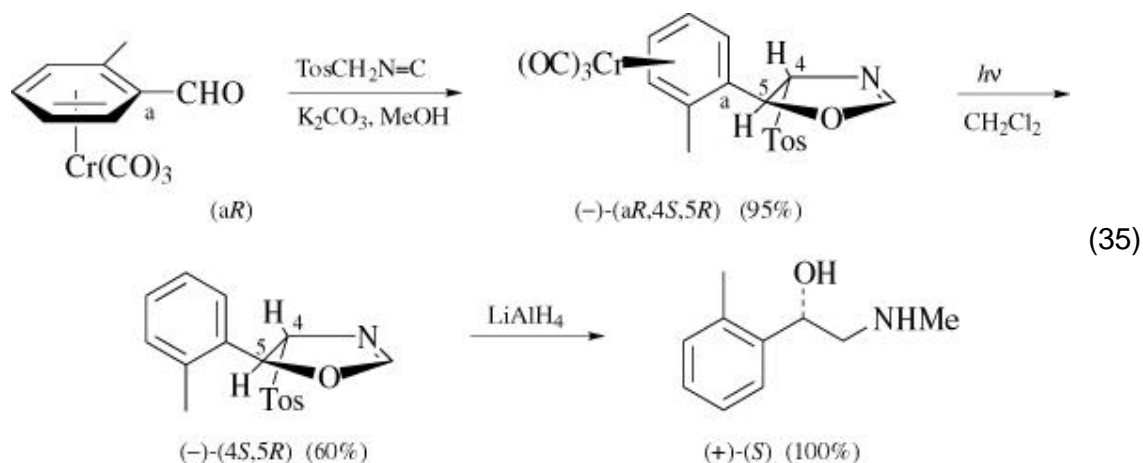
The reactions shown in Eqs. 32 and 33 form an efficient method for the introduction of 17-(hydroxyacetyl) side chains into 17-oxosteroids. (70, 71)

In a similar fashion, acid hydrolysis of 4-alkoxy-2-oxazolines **30** leads to α -hydroxy aldehydes (Eq. 34). (72)



Although 4-tosyloxazolines **28** can also be hydrolyzed by acid to afford α -hydroxy carbonyl compounds, (73) the 2- and 4-alkoxyoxazolines **29** and **30** are preferred precursors since they are more stable. (70)

Reduction of 4-tosyloxazolines **28** with LiAlH_4 leads to β -hydroxy *N*-methylamines. This reaction, which so far has been little investigated, applies to products derived from both ketones and aldehydes. The synthesis of β -hydroxy *N*-methylamines is exemplified by Eqs. 35 (74) and 37. (75)

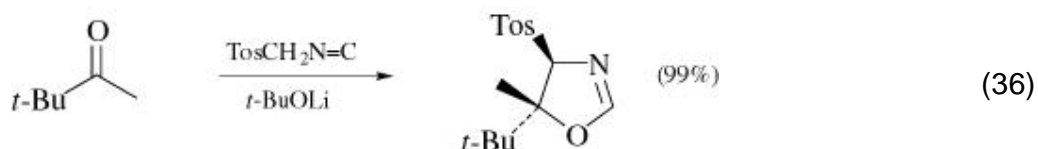


3.2. Stereochemistry

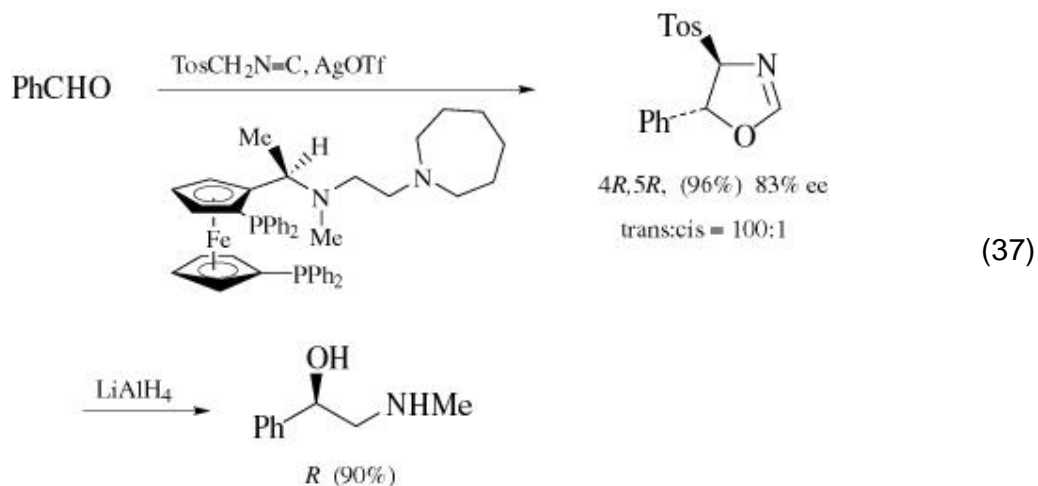
Several aspects of stereochemistry are involved in the reactions leading to oxazolines. The anion of TosMIC will attack sterically screened carbonyl groups from the least hindered side. For example, the (–)*aR* chromium complex of 2-methylbenzaldehyde is attacked by TosMIC anion exclusively from the side opposite to the (tricarbonyl)chromium group (Eq. 35), (74) and norbornanone is attacked exclusively from the exo side. (72)

4-Tosyloxazolines **28** may form cis/trans mixtures when $R^1 \neq R^2$. In the case of 4-tosyloxazolines derived from TosMIC and aldehydes, the dominant or

exclusive products have the *trans* configuration (as in Eq. 35), (36, 75) facile epimerization at C4 favoring the more thermodynamically stable product. (76) A comparable situation exists for tosyloxazolines derived from TosMIC and ketones (28, R³ = H). For example, only *trans*-5-*tert*-butyl-5-methyl-4-tosyl-2-oxazoline is formed in the reaction of TosMIC and *tert*-butyl methyl ketone (Eq. 36). (55, 77) Stereoselection in the formation of 2-alkoxy- and 4-alkoxyoxazolines 29 and 30 is less pronounced.



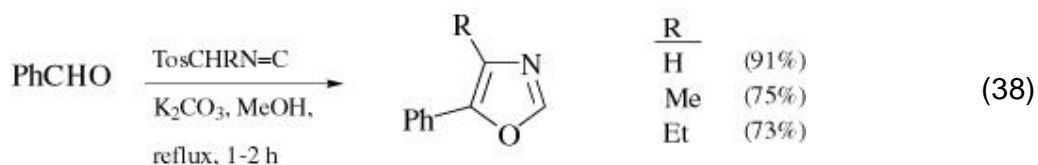
In a catalytic, asymmetric process related to Eq. 35, several aldehydes have been converted to *trans*-4-tosyloxazolines, with enantiomeric excesses ranging from 73 to 86%, by reaction with TosMIC under the influence of a chiral silver (I) catalyst derived from silver triflate and a *N, N, N'*, *N'*-tetraalkylethylenediamino-substituted bis(diphenylphosphino)ferrocene ligand (Eq. 37). (75)



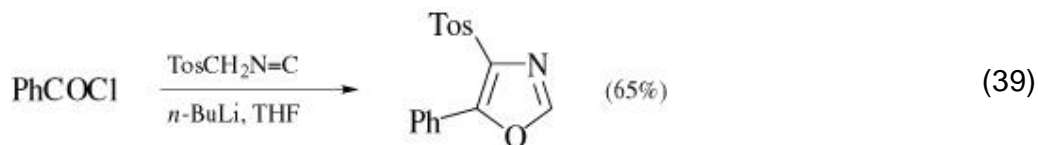
3.3. Oxazoles

Two types of oxazoles are accessible from TosMIC or monosubstituted TosMIC homologs. Reaction with aldehydes and base gives mono- or disubstituted oxazoles with a 5-aryl, 5-alkyl, or 5-hydrogen substituent, depending on the type of aldehyde used. A substituent R at the TosMIC

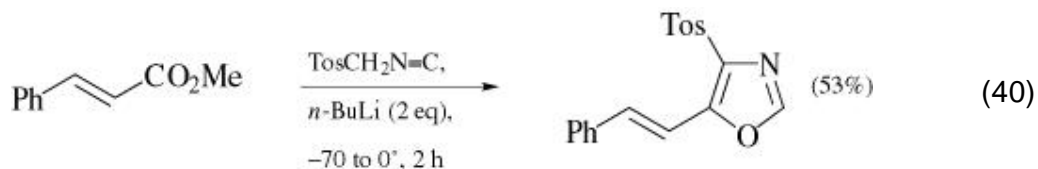
methylene group leads to a second substituent on the oxazole ring at C4 (Eq. 38). (26, 69, 78)



Reaction of TosMIC with acid chlorides or esters leads in a similar fashion to oxazoles which, however, always carry a tosyl group at C4 (Eq. 39). (26)



4-Tosyloxazoles are obtained similarly from carboxylic anhydrides and from selenol esters. Esters of aliphatic alcohols react with TosMIC only when two equivalents of *n*-butyllithium in THF are used (Eq. 40), the more nucleophilic dianion being necessary for attack at the ester carbonyl. (79)



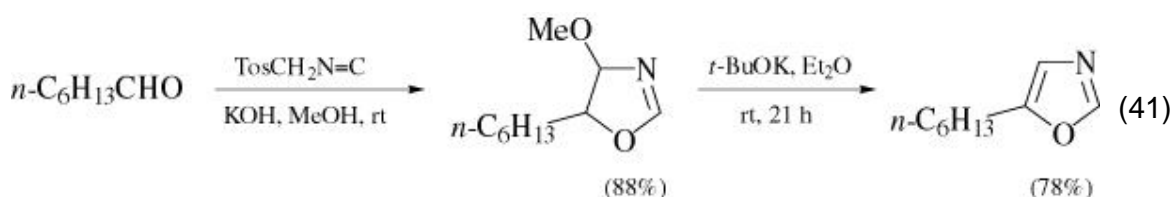
The example of Eq. 40 also shows that under the conditions given no reaction takes place at the conjugated double bond of the ester. With the softer monoanion of TosMIC, however, the reaction would take place exclusively at the C – C double bond. The latter reactions provide a highly useful synthesis of pyrroles, as is discussed in a later section.

In all cases, the oxazole ring carbon C2, originating from the isocyno group, remains unsubstituted (Eqs. 38–40). However, oxazoles with amino or alkoxy substituents at C2 are available by a related process using $\text{TosCH}_2\text{N}=\text{C}=\text{O}$

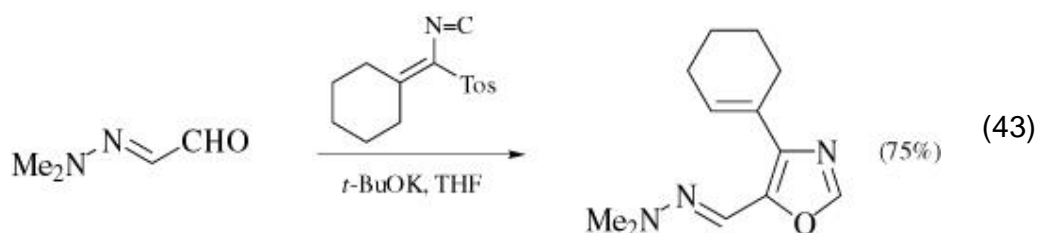
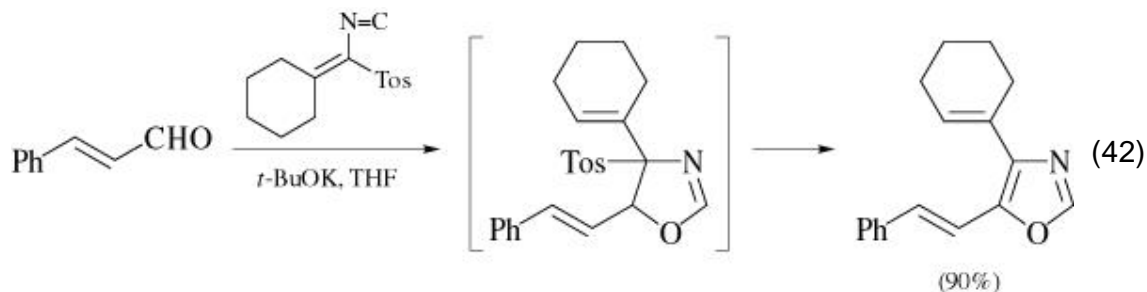
NR (46) and $\text{TosCH}_2\text{N}=\text{C}(\text{OR})$ (52) synthons, respectively, instead of TosMIC.

4-Tosyloxazolines of type **28** ($\text{R}^1 = \text{H}$) are the first-formed intermediates of Eq. **38** en route to oxazoles. Although oxazoles may be formed directly by base-induced elimination of TosH as suggested in Eq. **30**, it is not at all unlikely that alkoxyoxazolines **30** and/or **29** (Eq. **30**) are intermediates when the synthesis of oxazoles is carried out in alcoholic solvents. The oxazoles are formed eventually by elimination of R^4OH from **29** or **30** ($\text{R}^1 = \text{H}$). Several species of each of these potential intermediates have been isolated and characterized.

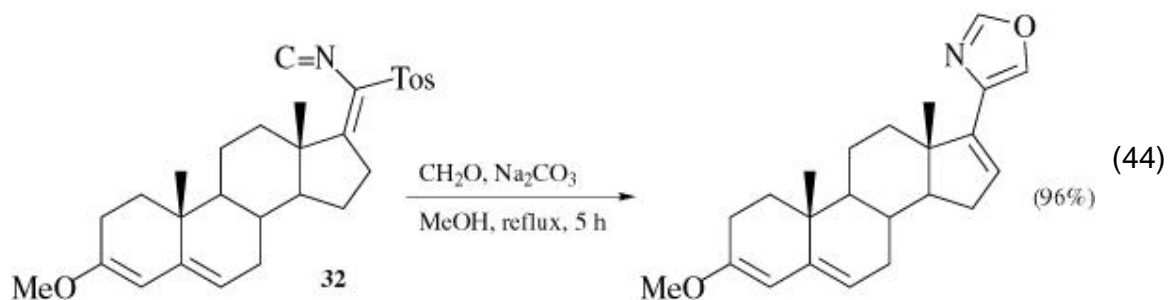
Whether alkoxyoxazolines **29** and **30** really occur as intermediates in the synthesis of oxazoles seems to depend in part on the relative acidities of the C4 and C5 hydrogens. For example, 5-hexyloxazole is formed only in 13% yield from TosMIC and *n*-heptanal, (**31**) whereas a 72% yield of 5-hexyl-4-methyloxazole is obtained when TosMIC is replaced by 1-tosylethyl isocyanide. (**31**) The low yield of 5-hexyloxazole is assumed to be a reflection of a larger difference in acidity between the hydrogens at C4 and C5 in the 4-tosyloxazoline precursor (see Eq. **30**), as compared to the corresponding species derived from benzaldehyde (Eq. **38**). In the latter reaction the increased acidity of the C5 hydrogen in the 4-tosyloxazoline precursor facilitates the base-induced elimination of TosH. The low yield of 5-hexyloxazole is improved by utilizing the two-step approach of Eq. **41**. The acidity of the C4 hydrogen is first decreased by replacing the tosyl group of the oxazoline precursor by a methoxy group, followed by elimination of methanol by *t*-BuOK in diethyl ether. (**31**)



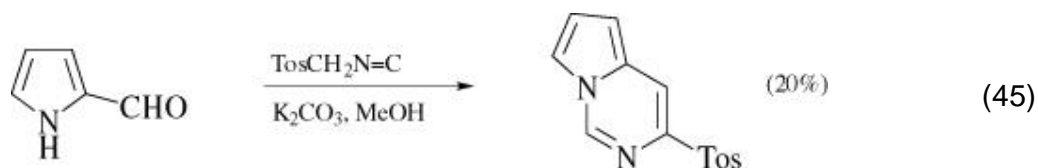
α , β -Unsaturated aldehydes react with TosMIC or monosubstituted TosMIC homologs at the aldehyde group to give oxazoles (Eq. **42**). (**80**) In a similar fashion, oxazoles are formed in reactions with α -keto aldehydes and with a hydrazone of glyoxal (Eq. **43**). (**63**)



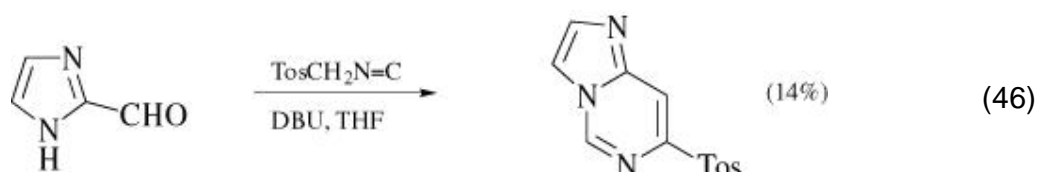
The reaction of Eq. 44 is one of the few examples of the conversion of formaldehyde into an oxazole. (70)



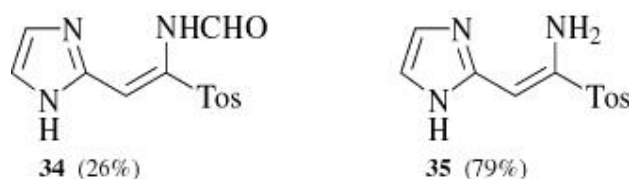
Only two aldehydes are reported to behave differently. Whereas 2-indolecarboxaldehyde forms an oxazole with TosMIC, (81) the reaction with 2-pyrrolicarboxaldehyde gives 3-tosylpyrrolo[1,2-*c*]pyrimidine (in low yield), through the participation of the pyrrole NH group in the ring-closing reaction (Eq. 45). (78)



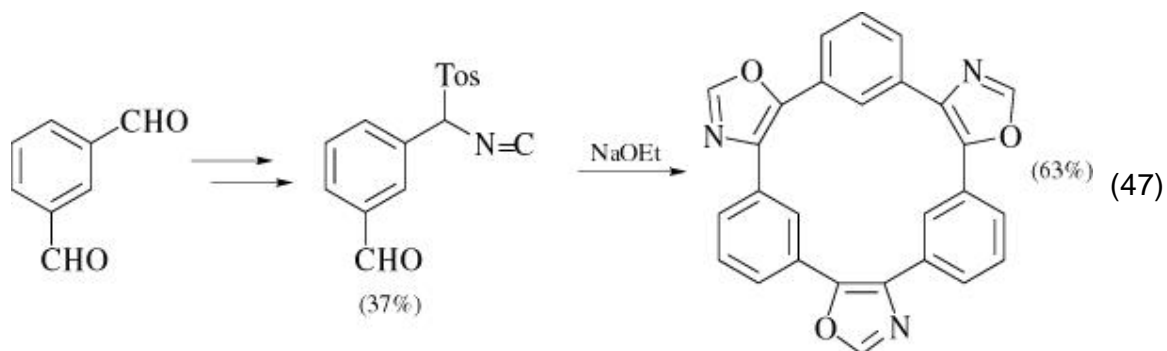
A similar pyrimidine, instead of an oxazole, is formed from 2-imidazolecarboxaldehyde and TosMIC (Eq. 46). (81) However, when the reaction conditions of Eq. 46 are changed to K_2CO_3 in methanol, products of ring opening of the expected

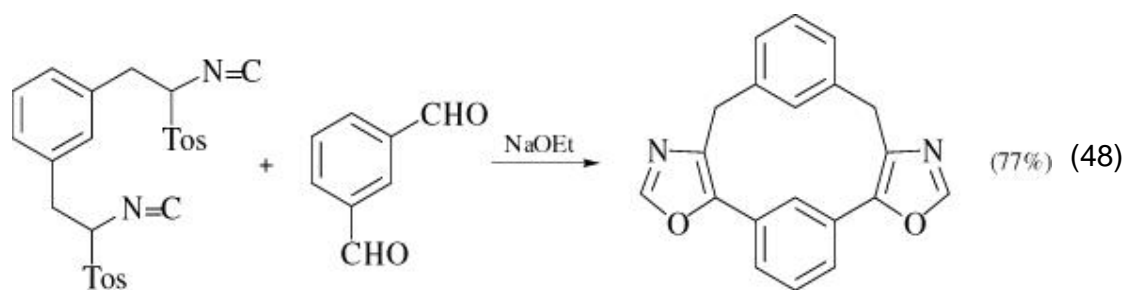


4-tosylloxazolines are formed (cf. Scheme 2): an unsaturated formamide **34** when the reaction is carried out at room temperature, and an unusual tosyl substituted primary enamine **35** at reflux temperature. (81)



Unusual examples of TosMIC oxazole syntheses are shown in Eqs. 47 (82) and 48. (83, 84)

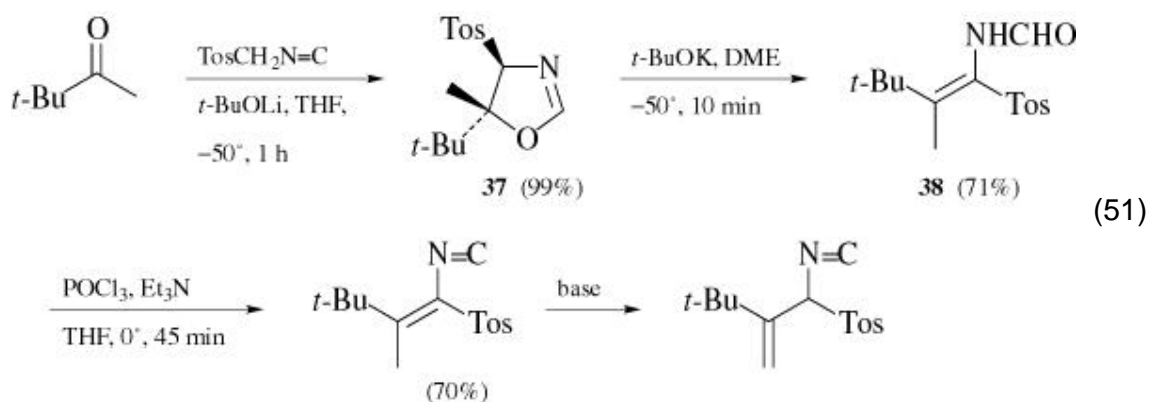




tetrahydrofuran at -70 to -40° for 30 minutes, followed by a quench with water and acetic acid. (63)

4.1. Scope and Limitations

The formal Knoevenagel condensation of TosMIC according to Eq. 49 is feasible with many different ketones and aldehydes. The limitations to the first reaction step are the same as in the reductive cyanation: no reaction occurs with severely sterically hindered ketones or with readily enolizable carbonyl compounds. With the less reactive, sterically screened carbonyl compounds exemplified by *tert*-butyl methyl ketone, the strenuous conditions necessary to realize the first reaction step also facilitate subsequent steps, leading to reductive cyanation. This problem was solved by carrying out the conversion to the unsaturated formamide in two separate steps (Eq. 51). (55)



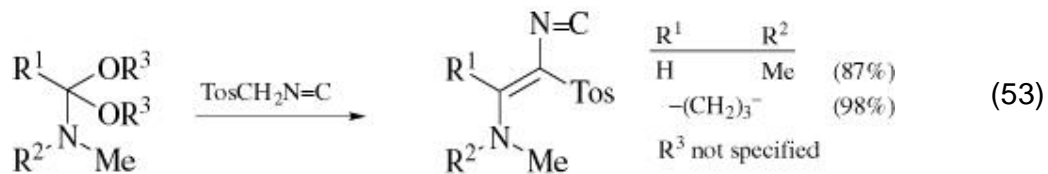
First, 5-*tert*-butyl-5-methyl-4-tosyl-2-oxazoline (37) is formed by reaction in tetrahydrofuran, using lithium *tert*-butoxide. The ring opening to (*E*)-*N*-(2,3,3-trimethyl-1-tosyl-1-butenyl)formamide (38) is then carried out under mild conditions using potassium *tert*-butoxide in 1,2-dimethoxyethane at -50° . This approach is also recommended for other less reactive carbonyl compounds.

When cis/trans isomers are possible, as with aldehydes and unsymmetrical ketones, single stereoisomers are formed almost without exception. The bulkier groups are assumed to be trans to the tosyl group, as in the established structure (88) of the isocyanide derived from pivalaldehyde. (86)

The Peterson olefination approach is applicable only to aldehydes and activated ketones, such as cyclobutanone. With aldehydes, the best results are obtained with non-enolizable compounds such as cinnamaldehyde (Eq. 52). (87)



Two examples of a direct condensation of amido acetals and TosMIC have been reported briefly (Eq. 53). (89)



5. TosMIC Substituted at the Methylene Group

Both mono- and disubstituted TosMIC derivatives are well known, substituents most commonly being alkyl or aralkyl.

5.1. Monosubstituted TosMIC Derivatives

Normally, the reaction of TosMIC with one equivalent of an alkylating agent leads to mixtures of starting material with mono- and dialkylated products. When monosubstitution of TosMIC is desired, phase transfer catalysis (PTC) is the method of choice, as in Eq. 54.

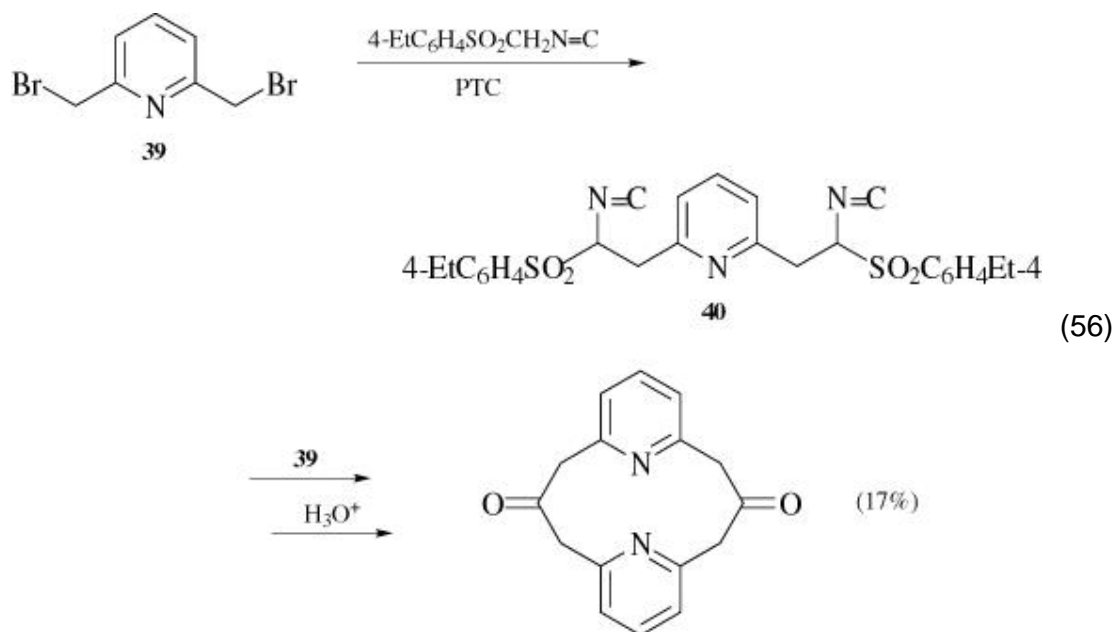


Benzyltriethylammonium chloride (BTEAC), tetrabutylammonium bromide (TBAB), and tetrabutylammonium iodide (TBAI) have been commonly employed for these reactions, in a mixture of dichloromethane and 20–50% aqueous sodium hydroxide. High yields are normally obtained from primary bromides or iodides, and also from benzyl bromide or allyl chloride. (Eq. 55). (73, 90, 91)



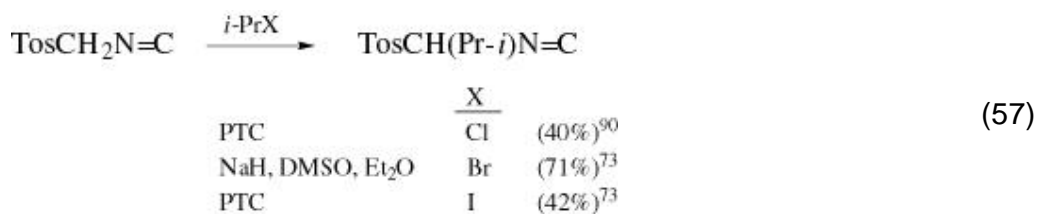
1-Tosylethyl isocyanide has been prepared by monomethylation of TosMIC (Eq. 54). (90, 91) The same compound is also available from the Mannich route (Eq. 16). (90)

Benzylic-type monoalkylation has been used in a double fashion to form compound 40 as part of a synthesis of cyclophanes (Eq. 56). A TosMIC analog (4-ethylphenylsulfonylmethyl isocyanide) was used in this sequence. (92)



In addition to 1-tosyl-3-butenyl isocyanide (Eq. 55), only two other examples are known of monosubstituted TosMIC derivatives specifically functionalized at the β position: (1) with a trimethylsilyl group (91, 93) and (2) with an ester group. (91)

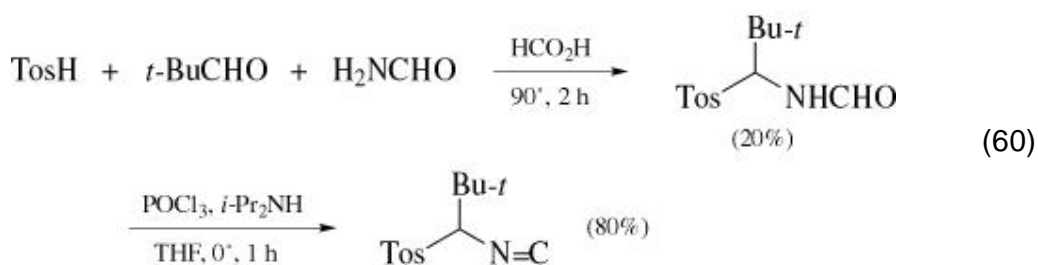
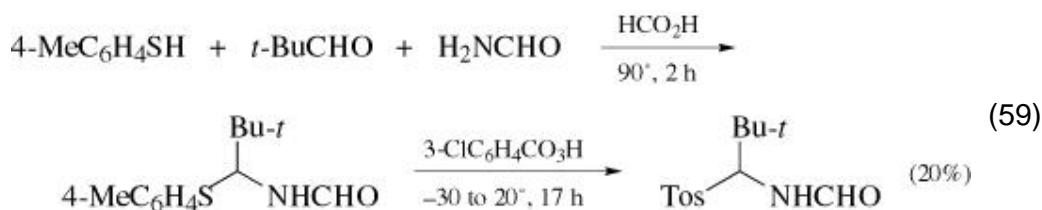
The yields of monoalkylations with secondary alkyl halides tend to be lower than with primary halides (Eq. 57).



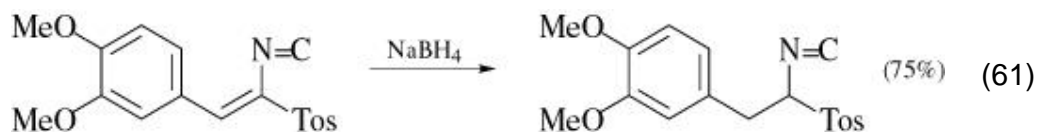
Better results are sometimes obtained with secondary alkyl bromides or iodides when sodium hydride in a mixture of dimethyl sulfoxide and diethyl ether is employed (Eq. 58). (73)



As expected, the reaction of *tert*-butyl bromide or iodide with TosMIC does not lead to 2,2-dimethyl-1-tosylpropyl isocyanide. This compound has been prepared in two different ways by the Mannich approach (Eqs. 59 and 60). (94)

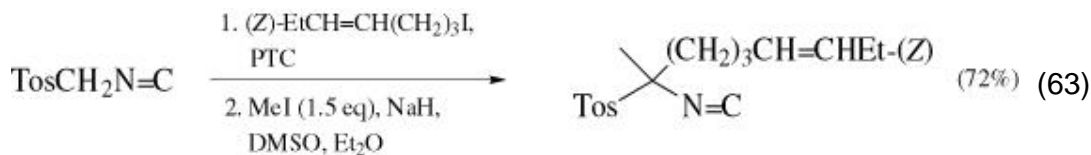
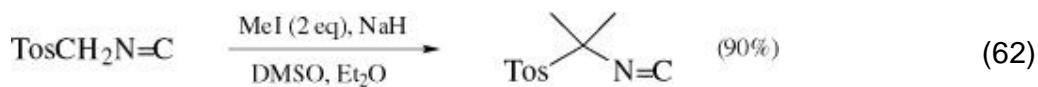


Sodium borohydride reduction of the formal Knoevenagel condensation products of TosMIC and aldehydes or ketones also leads to monosubstituted TosMIC derivatives (Eq. 61). (45, 95, 96)



5.2. Disubstituted TosMIC Derivatives

Dialkylation of TosMIC is readily achieved by using two equivalents of alkylating agent. Such reactions are usually carried out by using sodium hydride in a dimethyl sulfoxide—diethyl ether mixture (Eqs. 62 and 63). (35, 97)

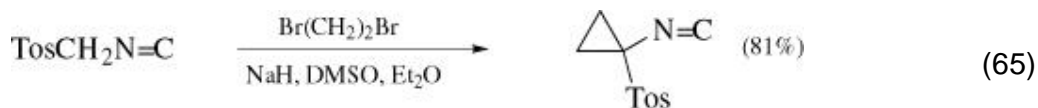


Dialkylated compounds cannot be synthesized by the Mannich approach because of the instability of the formamido-precursors $\text{TosCR}^1\text{R}^2\text{NHCHO}$ when both R^1 and R^2 are not hydrogen. (98) The only exceptions are 1-tosyl-1-formamidocyclopropanes. (99)

The best results in the dialkylation of TosMIC are usually obtained with primary alkyl bromides or iodides, and with allylic or benzylic chlorides or bromides. Although PTC conditions are used in particular for monoalkylations, the same conditions have been used occasionally for the introduction of a second alkyl group. Under appropriate conditions even a less reactive halide, such as the chlorine in Eq. 64, may remain untouched. (100) Nevertheless, alkyl chlorides have been used successfully at slightly elevated temperatures and/or prolonged reaction times. (101)

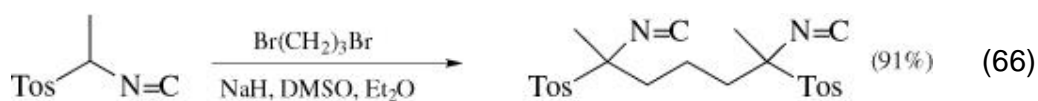


Dibromides or diiodides react with TosMIC to form ring systems by intramolecular dialkylation (Eq. 65). Simple 1,n-dibromides (or iodides) have been used to form 3- to 7-membered rings. (39, 73, 102)

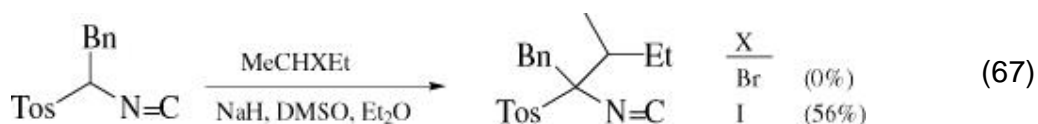


Monosubstituted TosMIC derivatives react with 1,n-dihalides to afford

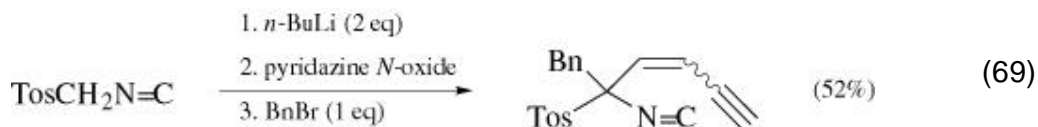
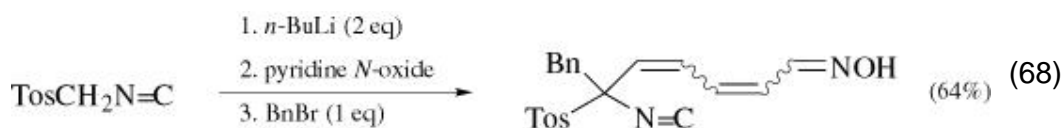
dialkylation products (Eq. 66). (100) Bridges of 2 to 9 atoms have thus been realized.



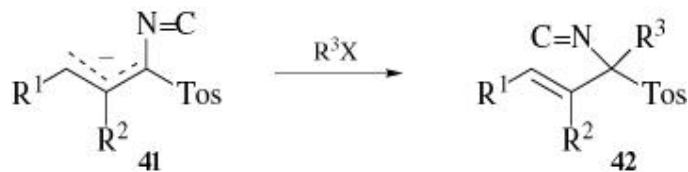
Lower yields obtained in the reactions with 1,2-dibromoethane or 1,2-diiodoethane may reflect steric hindrance, which is compounded with 2-phenyl-1-tosylethyl isocyanide. The latter fails to react with 1,2-dibromoethane and requires an iodide for introduction of a sec-butyl group (Eq. 67). (73, 100)



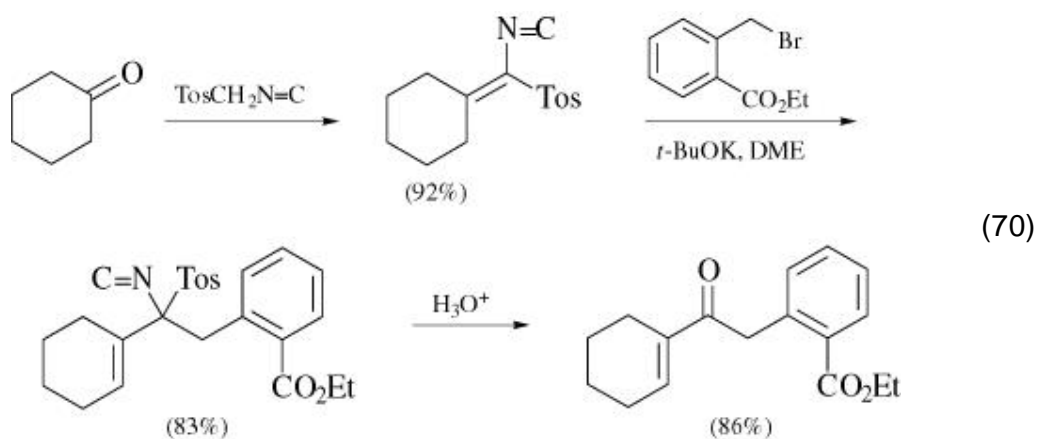
Two unusual disubstituted TosMIC derivatives have been obtained from the reaction of dilithio-TosMIC with pyridine-*N*-oxide and with pyridazine-*N*-oxide, followed by benzylation (Eqs. 68 and 69). (79)



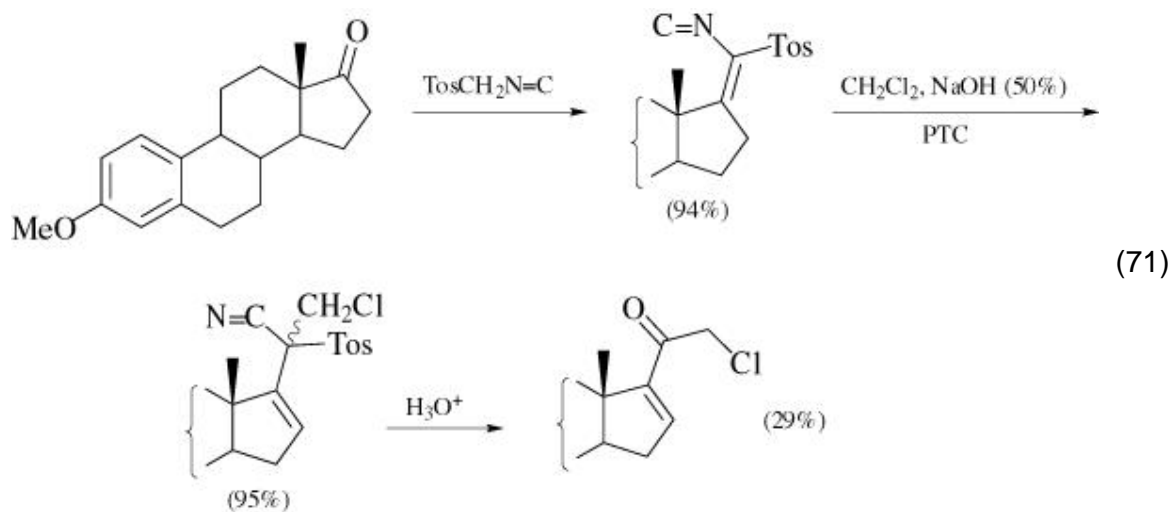
A more general method for the synthesis of TosMIC derivatives **42** with a 1-alkenyl substituent involves alkylation of allylic anions **41**, formed by γ deprotonation of the (formal) Knoevenagel condensation products of TosMIC and ketones. These alkylations take place exclusively at C1. (101, 103)



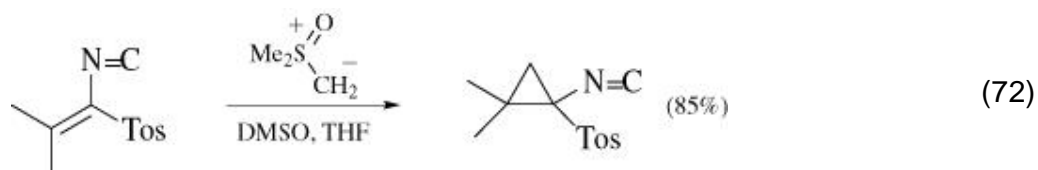
The allylic alkylation reaction **41** \rightarrow **42** forms part of a widely applicable conversion of ketones to homologous enones, as in Eq. 70. (103)



The same approach, using dichloromethane in the alkylation step, is used for the introduction of functionalized acetyl side chains at C17 in 17-oxosteroids (Eq. 71) (101)



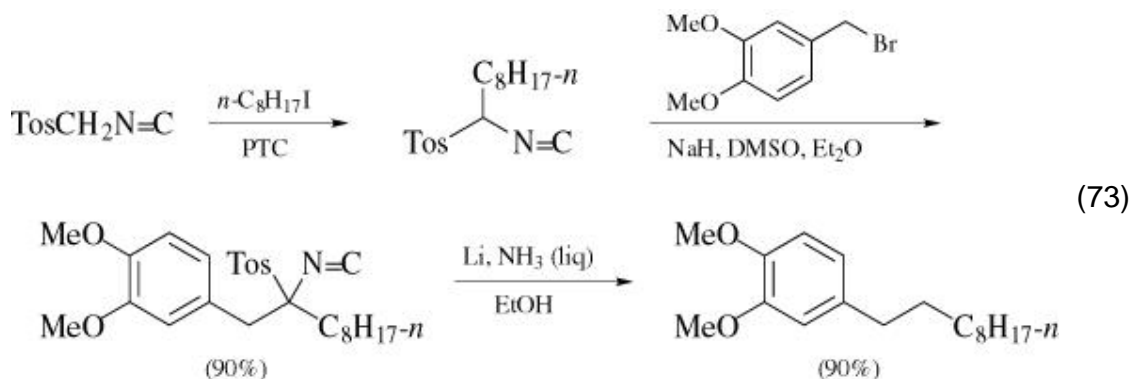
A methylene transfer reaction, using dimethyloxosulfonium methyliide, applied to the (formal) Knoevenagel condensation product of TosMIC and acetone leads to a cyclopropane derivative (Eq. 72). (102)



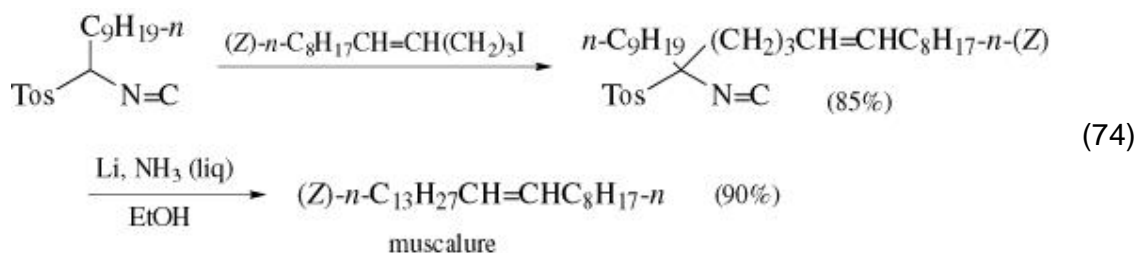
5.3. TosMIC as a Connective Reagent

In the reactions discussed so far, TosMIC is used to connect two (ar)alkyl halides, either inter- or intramolecularly, by a functionalized methylene bridge. Hence, TosMIC here fulfills the role of a connective or conjunctive reagent. (104) Practical applications of this type of TosMIC reaction derive from the various ways in which the geminal isocyano and tosyl groups in the products can be subsequently transformed. Most prominent among these transformations is acid hydrolysis to a keto group, as in Eqs. 13, 70, and 71. Details of this hydrolysis are discussed in the section on the TosMIC-based synthesis of ketones.

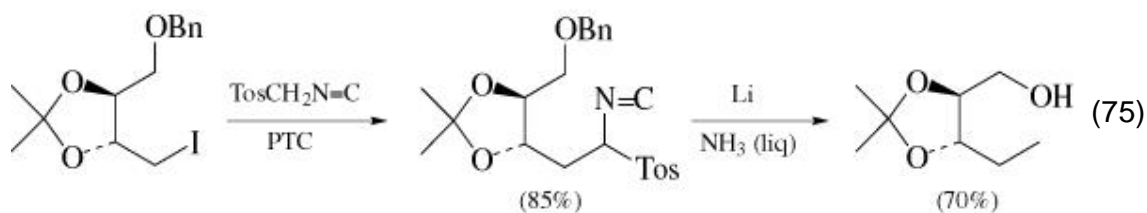
The remaining part of this section emphasizes the use of TosMIC to form methylene bridges. The geminal isocyano and tosyl groups are directly converted to a methylene group by reduction with lithium in liquid ammonia containing 3 equivalents of ethanol. (105, 106) Thus, the combination of TosMIC dialkylation followed by Li/ NH₃ reduction makes TosMIC a CH₂ connector of two alkyl halides, as in Eq. 73. (105)



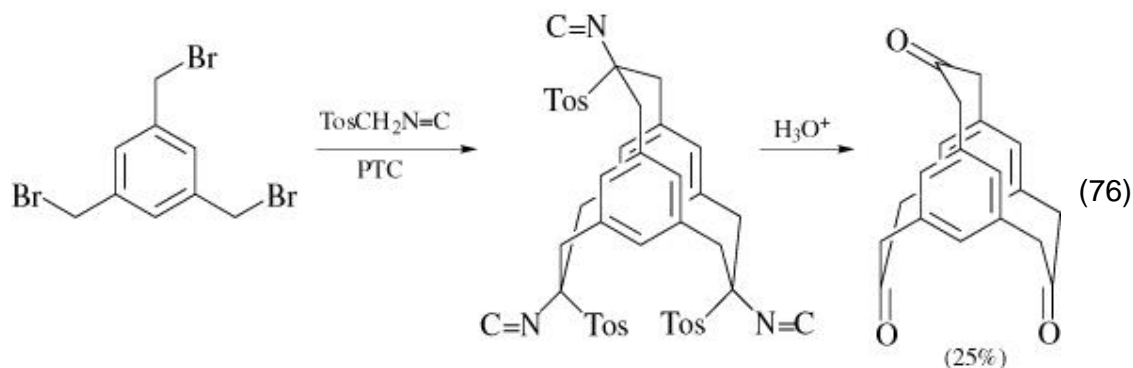
This approach has been used for the synthesis of muscalure (a pheromone of the common housefly) by using TosMIC as a CH₂ connector: (1) between *n*-nonyl bromide and (*Z*)-tridec-4-enyl iodide (Eq. 74); (105, 106) (2) between *n*-butyl iodide and the iodide derived from oleic acid. (107)

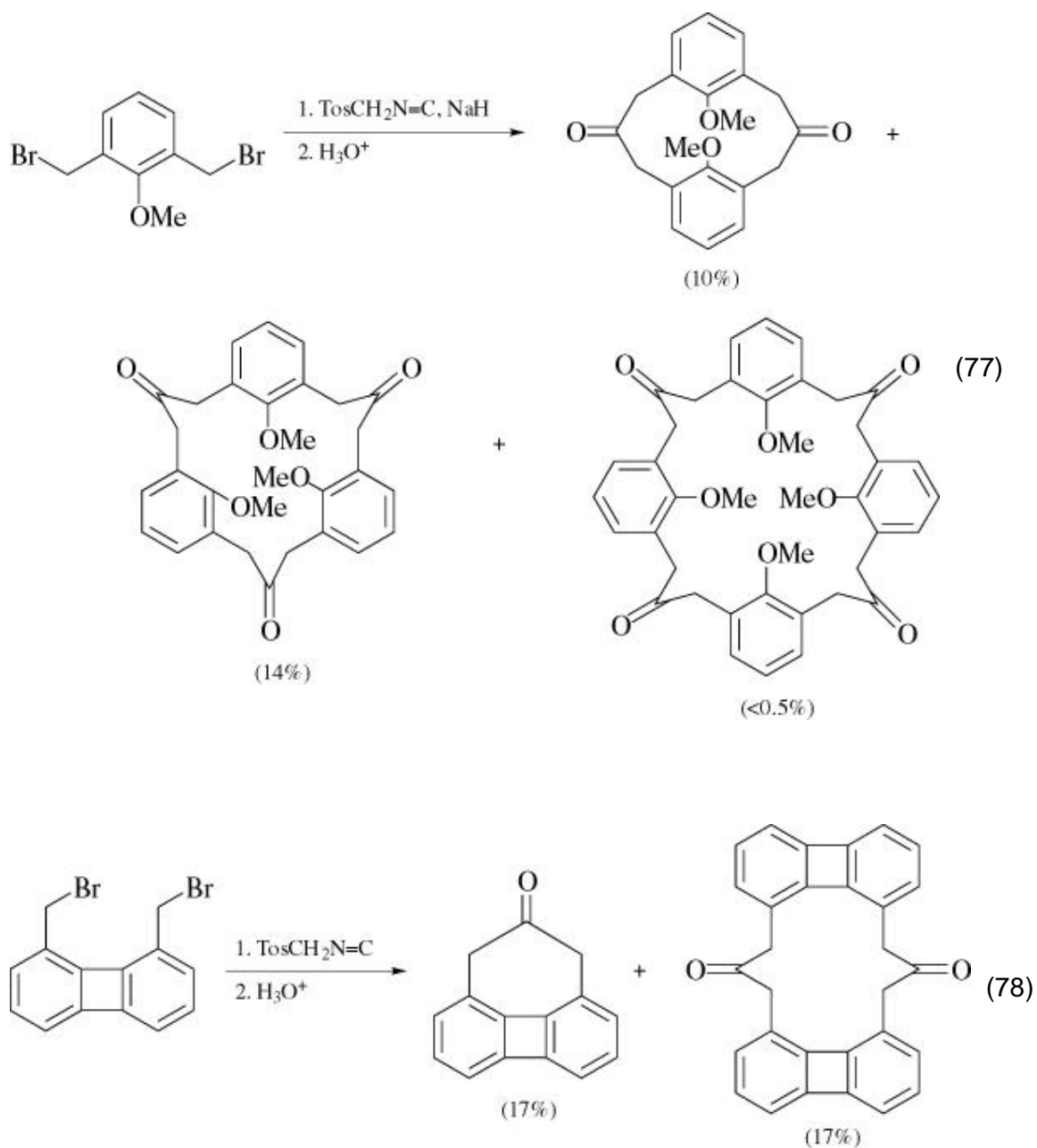


Reduction of a monosubstituted TosMIC derivative forms a methyl group (Eq. 75). (105) Alternative reduction products which may be obtained from TosMIC derivatives are discussed later.



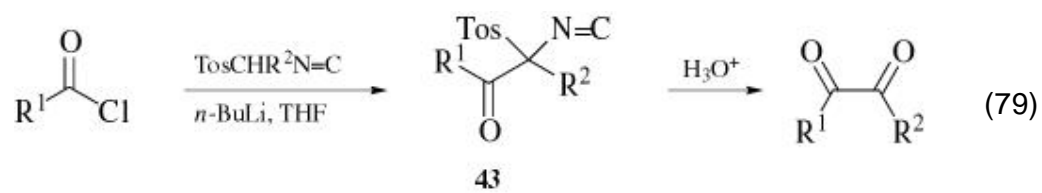
The dibenylation of TosMIC has been used extensively to form large ring systems, in particular various cyclophanes (Eqs. 76–78). (108-111)





5.4. Acylated TosMIC Derivatives

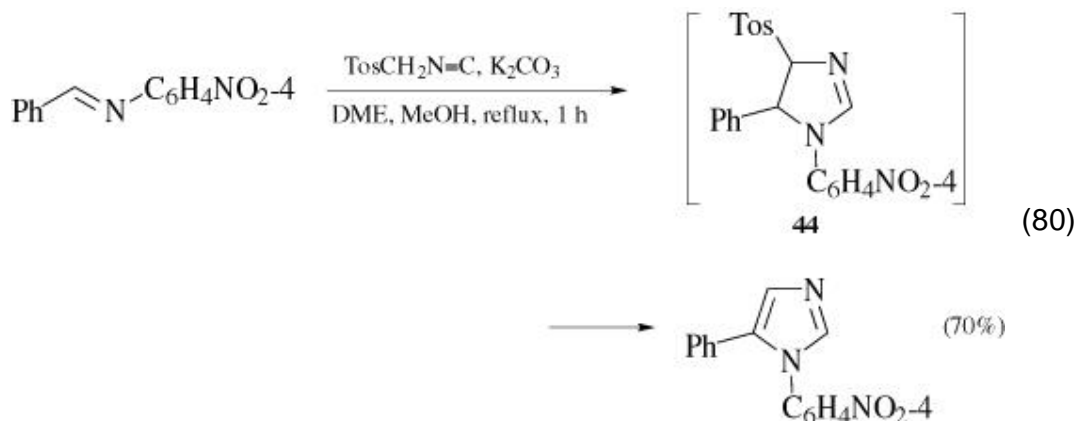
Reaction of monosubstituted TosMIC derivatives with acyl halides leads to disubstituted TosMIC compounds **43** carrying one acyl group, as in Eq. 79. (112) The products **43** are precursors of 1,2-diketones, which are formed upon acid hydrolysis. The acylation reaction is restricted to monosubstituted TosMIC derivatives, since the corresponding reaction with TosMIC leads to oxazoles.



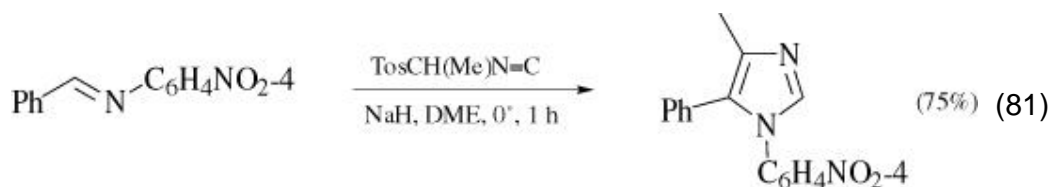
6. Synthesis of Imidazoles and 1,2,4-Triazoles

6.1. Imidazoles

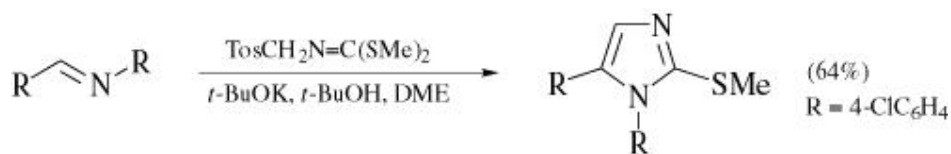
The synthesis of imidazoles from imines and TosMIC or TosMIC homologs is closely related to the previously discussed synthesis of oxazoles from carbonyl compounds, but has not been as extensively investigated. No reports are available on reactions of ketimines, but the reaction of aldimines with TosMIC and base provides 1,5-disubstituted imidazoles in variable yields (Eq. 80). (37)



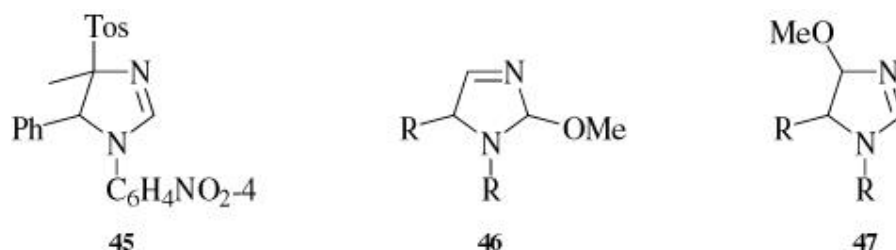
1,4,5-Trisubstituted imidazoles are formed similarly when TosMIC is replaced by a homolog, as in Eq. 81. (37, 69)



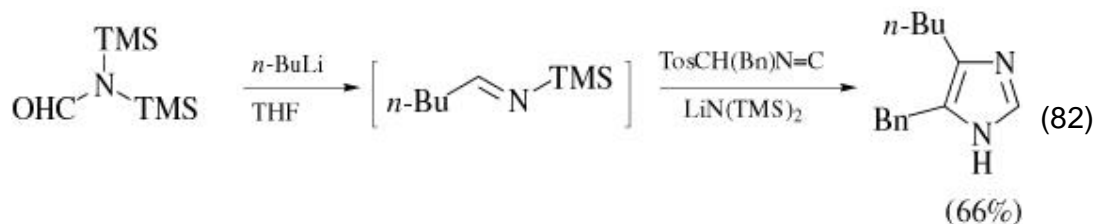
Some 1,2,5-trisubstituted imidazoles have been prepared with the use of (formal) TosMIC derivatives $\text{TosCH}_2\text{N}=\text{C}(\text{SCH}_3)\text{R}$ ($\text{R} = \text{C}_6\text{H}_5, \text{CH}_3\text{S}$), which provide a phenyl or a methylthio group at the 2-position. (47)



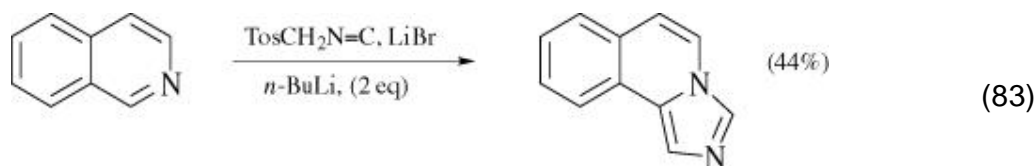
Intermediate 4-tosylimidazolines have been isolated in a few cases only. 4-Tosylimidazoline **44**, for example, is obtained in 73% yield when the reaction of Eq. **80** is carried out with sodium hydride in 1,2-dimethoxyethane in the absence of methanol at -20° . (**37**) Under these conditions, however, no tosylimidazoline **45** is obtained from the reactants of Eq. **81**. It is not known whether 4-toluenesulfonic acid is eliminated directly from 4-tosylimidazolines like **44**, or that methoxyimidazolines of type **46** and/or **47** are involved. In contrast to the oxazoline series, such methoxyimidazolines have not been identified.



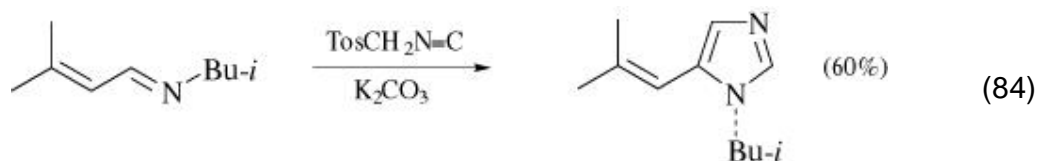
N-(Trimethylsilyl)aldimines react with TosMIC derivatives to produce *N*-unsubstituted imidazoles (Eq. **82**). (**113**)



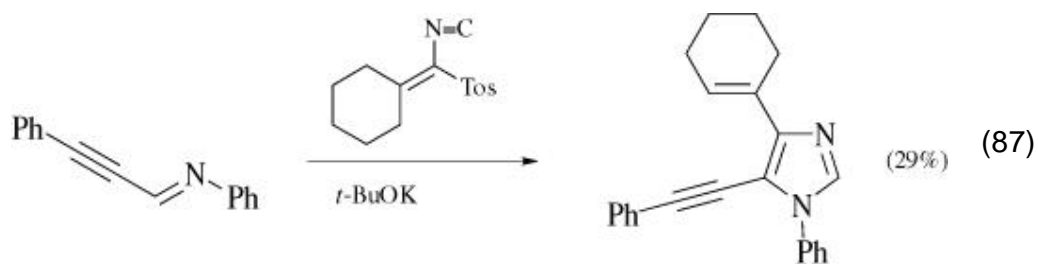
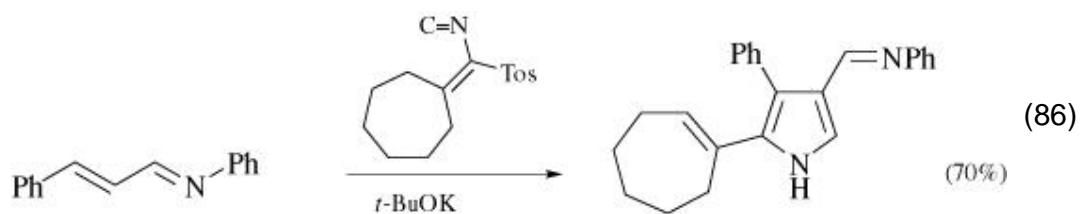
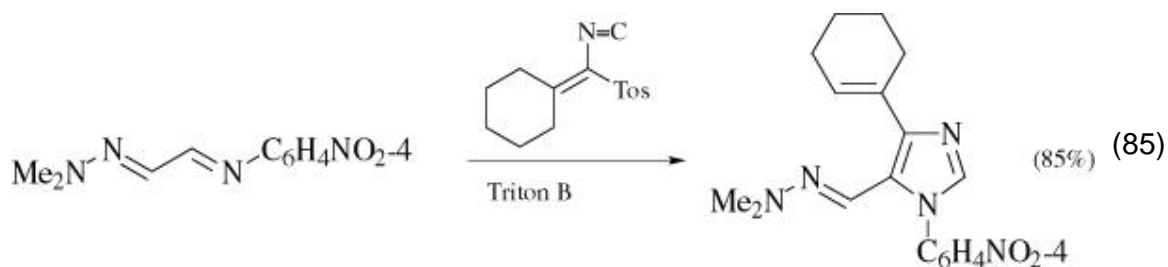
The C — N double bonds of quinoline, isoquinoline, quinazoline, (**79**) and 4*H*-pyrrolo[1,2-*a*][1,4]benzodiazepine (**8**) are also subject to the formation of imidazoles, as in Eq. **83**, but only when the more nucleophilic reagent dilithio-TosMIC is used. This type of reaction fails with pyridine or pyridazine. (**79**)



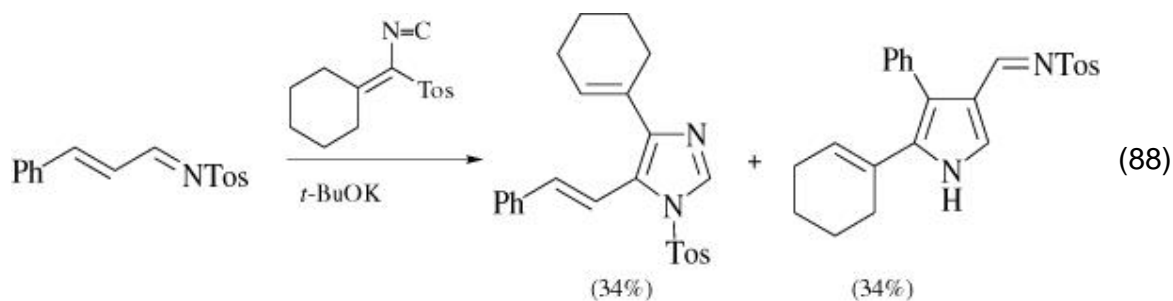
β -Unsaturated aldimines usually form imidazoles (114, 115) (Eq. 84), although reaction with the C — C double bond occasionally leads to pyrrole formation.



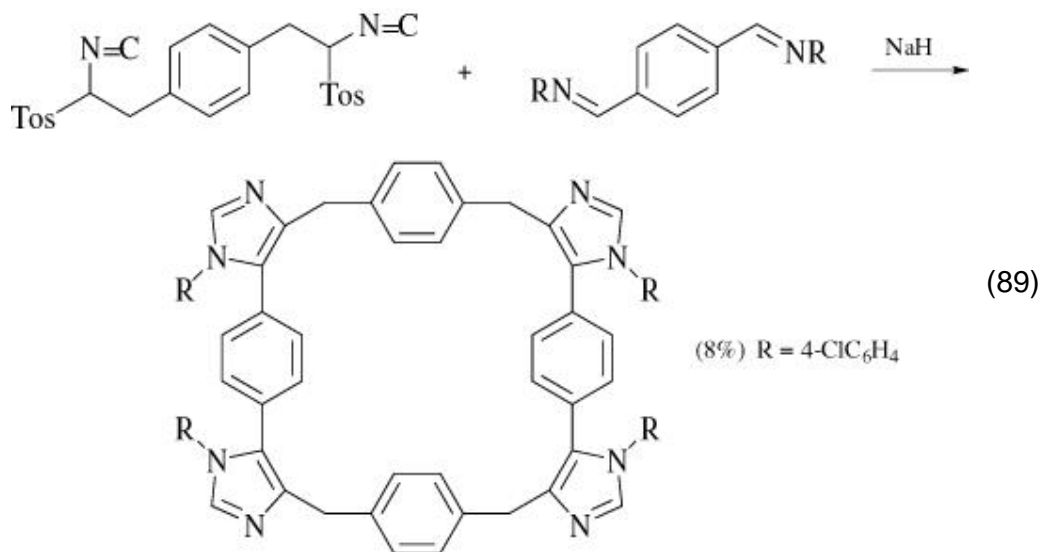
Imidazoles are formed similarly by reaction of the 4-nitrophenylimine of cinnamaldehyde and of a hydrazone derivative of glyoxal with a TosMIC homolog derived from cyclohexanone (Eq. 85). (63, 80) On the other hand, a pyrrole is formed from the phenylimine of cinnamaldehyde and an analogous 7-ring TosMIC homolog (Eq. 86). (80) The formation of pyrroles is avoided by replacing the C — C double bond by a triple bond (Eq. 87). (80)



A 1:1 mixture of imidazole and pyrrole is obtained in the reaction of the *N*-tosylimine of cinnamaldehyde (Eq. 88). (80)



An interesting application of the TosMIC imidazole synthesis is depicted in Eq. 89, where four imidazole rings are formed in one operation.

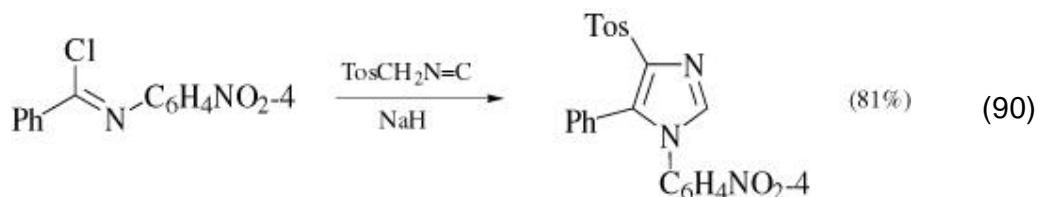


A base-induced conversion of a bis(imine) derived from phthalic dicarboxaldehyde and the reaction product of 1,4-(dibromomethyl)benzene and two molecules of TosMIC gives a paracyclophane as a 2:2 reaction product. (116)

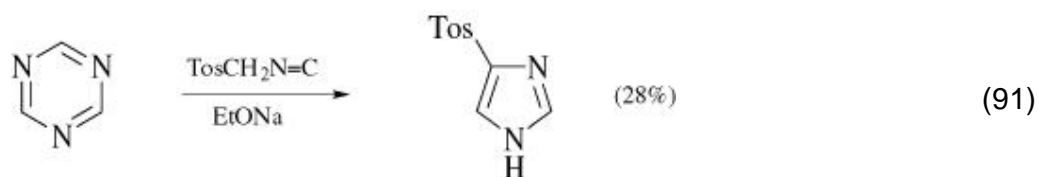
The majority of imidazoles have been prepared by the reaction of aldimines derived from aromatic aldehydes and aliphatic amines. This protocol also applies to aldimines derived from aliphatic aldehydes and aliphatic amines, as well as aromatic aldehydes and aromatic amines. However, the method seems

to fail with aldimines derived from aliphatic aldehydes and aromatic amines. (77)

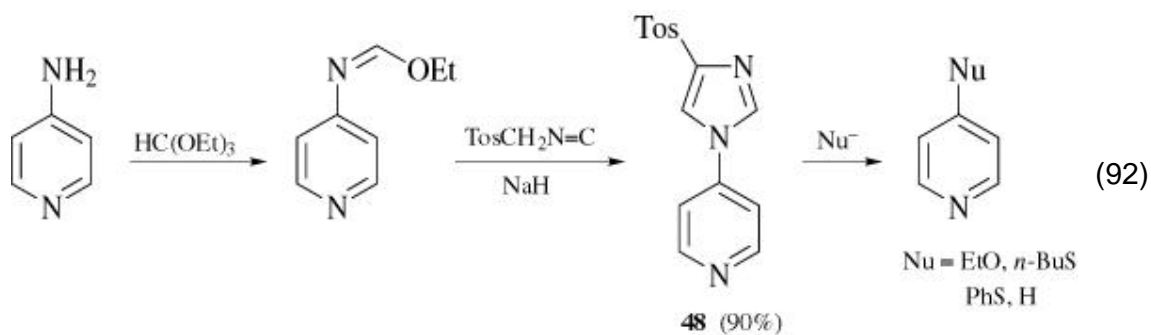
The reaction of imidoyl chlorides and TosMIC leads to 4-tosylimidazoles (Eq. 90). (37, 77)



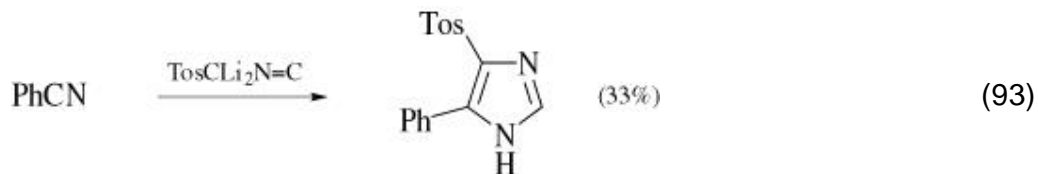
Leaving groups other than chloride have been used occasionally: the diethyl phosphonate group in the reaction of a benzodiazepine derivative (117) and an amino fragment in the reaction of TosMIC with *sym*-triazine (Eq. 91). (118)



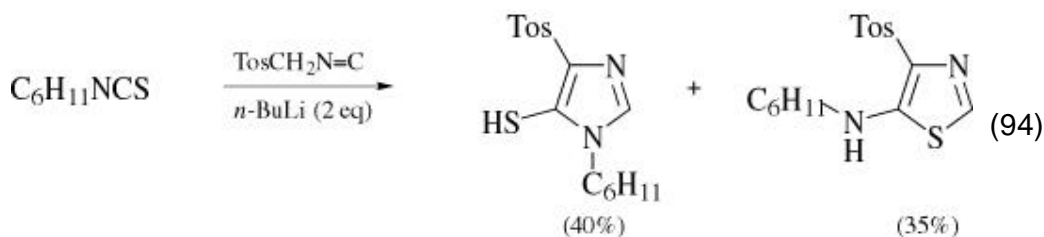
Formimidates have been used similarly for the synthesis of 4-tosylimidazoles such as 48. The tosylimidazolyl group in compound 48 may then be used as a leaving group to effect the net nucleophilic displacement of amino groups from the heterocycle (Eq. 92). (119)



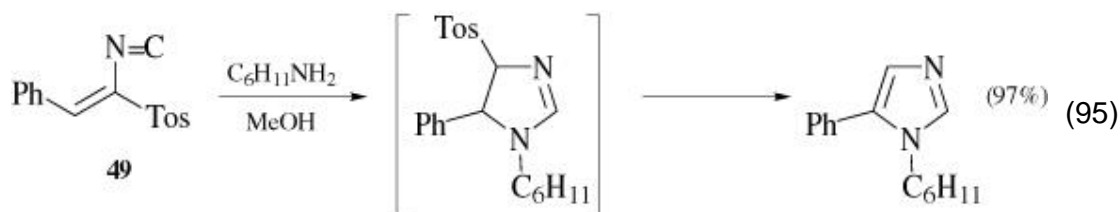
One example describes the formation of an imidazole from a nitrile and dilithio-TosMIC (Eq. 93). (79)



The reaction of TosMIC with isothiocyanates may lead to 4-tosylimidazoles, although 4-tosylthiazoles are also formed, as shown in Eq. 94. When the same reaction is carried out with sodium hydride in 1,2-dimethoxyethane at 0°, the thiazole is obtained as the sole product in 76% yield. (120)



An alternative way to synthesize imidazoles involves the addition of amines to 1-isocyano-1-tosyl-1-alkenes (Eq. 95). The reaction is limited to the use of aliphatic primary amines and ammonia; aniline is not sufficiently nucleophilic to react. (86)

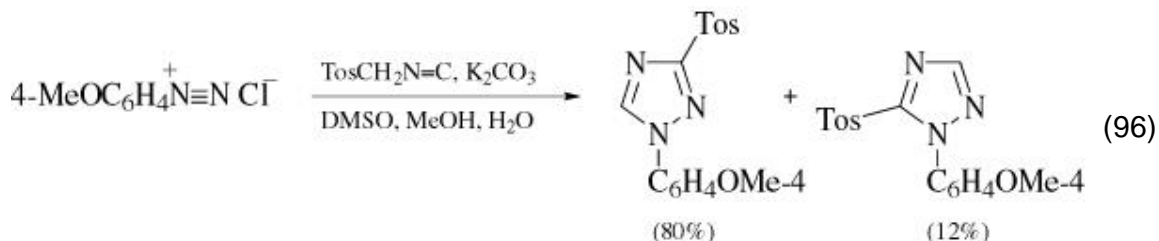


It should be emphasized that the essential difference between the two synthetic approaches to imidazoles merely is a matter of sequence in which

the three basic reaction partners—TosMIC, aldehyde, and amine—are brought together. In the approach of Eq. 80 an aldimine is prepared first (from an aldehyde and amine) which then reacts with TosMIC, whereas in the procedure of Eq. 95 TosMIC is reacted first with an aldehyde (e.g., benzaldehyde) to give 49 which is followed by reaction of the product with an amine. The two approaches, however, do not cover the same range of products. The first method allows, through the use of TosMIC homologs, the synthesis of 1,4,5-trisubstituted imidazoles (Eq. 81), which are not otherwise accessible. 5-Monosubstituted imidazoles are available by using ammonia in Eq. 95; the same imidazoles require the use of *N*-trimethylsilyl aldimines in the first approach of Eq. 82. As was mentioned before, the second approach (Eq. 95) does not seem to apply to aromatic amines, whereas the first one does. Where both methods have been applied to the synthesis of the same imidazole, the second approach seems to give the higher yields. (86) The aldimines used in the first approach (Eq. 80) may be formed in situ. (121)

6.2. 1,2,4-Triazoles

One report describes the synthesis of 1,2,4-triazoles by a base-induced cycloaddition of TosMIC to diazonium salts (Eq. 96). (122)

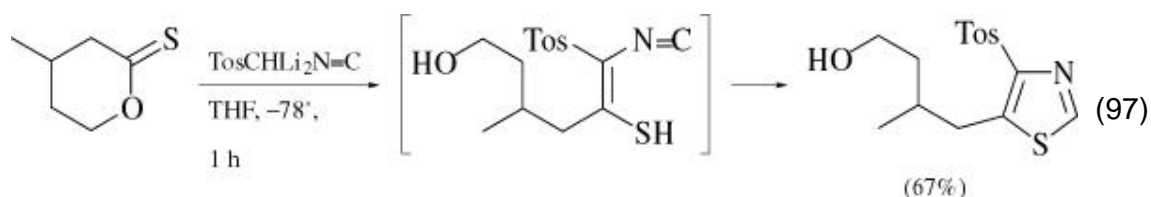


The reaction fails with 4-nitrophenyldiazonium tetrafluoroborate, which reacts with TosMIC anion via displacement of the diazonium group. (122)

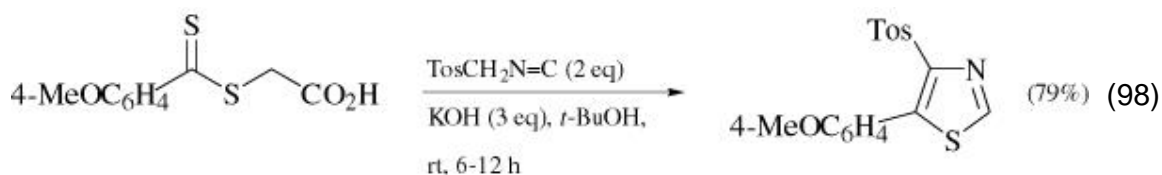
7. Synthesis of Thiazoles from Thiocarbonyl

Compounds

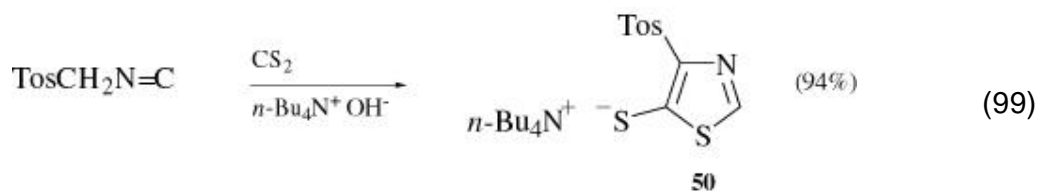
Thiazoles are formed by base-induced cycloadditions of TosMIC to the C=S double bond of various thiocarbonyl compounds. The thiocarbonyl substrates used so far have led to 4-tosyl substituted thiazoles only, as in the reaction of a thionolactone (Eq. 97). (123)



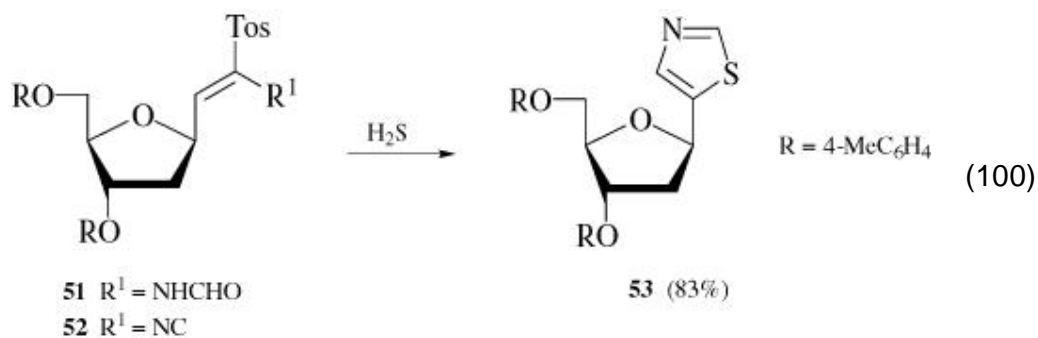
In the mechanism shown in Eq. 97, the alkoxy group departs upon attack of TosMIC anion, prior to α -addition of the tautomeric thioenol function to the isocyano carbon; a concerted addition to the thiocarbonyl group is also possible. (123, 124) The corresponding reaction of acyclic thiono esters ($\text{RC}(=\text{S})\text{OR}'$) and dithiono esters ($\text{RC}(=\text{S})\text{SR}'$) appears to fail, unless the leaving group in the dithio esters is activated by the use of $\text{R}\phi = \text{CH}_2\text{CO}_2\text{H}$ or $\text{CH}_2\text{CO}_2\text{R}^2$. Eq. 98 gives an example. (124)



Addition of TosMIC anion to the thiono group of cumulated systems also leads to the formation of 4-tosylthiazoles. The reaction with carbon disulfide gives 5-thio-4-tosylthiazoles as in Eq. 99. Most 4-thio-5-tosylthiazoles **50** have only been isolated and characterized after in situ alkylation or acylation of the thiolate group. (125)



A 4-unsubstituted thiazole is obtained in a process not based on the use of a thiocarbonyl substrate (Eq. 100). (126) Formamide **51** is dehydrated in the usual way to α , β -unsaturated tosyl isocyanide **52**, which by addition of hydrogen sulfide gives thiazole **53**.



No reactions of TosMIC with thioaldehydes or thioketones have been reported.

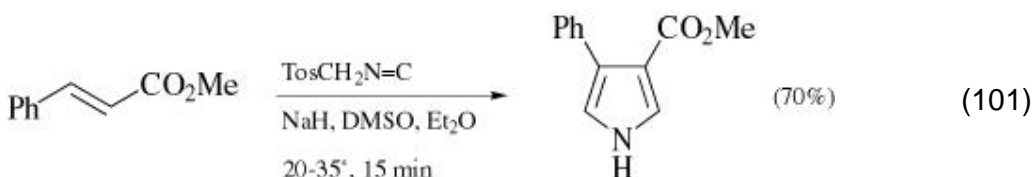
8. Synthesis of Pyrroles and Indoles

The preparation of pyrroles constitutes one of the major synthetic uses of TosMIC, and a variety of substituent types and patterns can be accessed. Three reactants are needed: TosMIC, an aldehyde, and a compound with an activated methyl or methylene group. In practice, the TosMIC-based synthesis of pyrroles is not carried out as a three-component reaction. Two reaction modes are possible (Scheme 4): (1) a base-induced reaction of TosMIC with a Michael acceptor molecule [54](#), and (2) a base-induced reaction of an activated methyl compound with a 1-isocyano-1-tosyl-1-alkene [55](#).

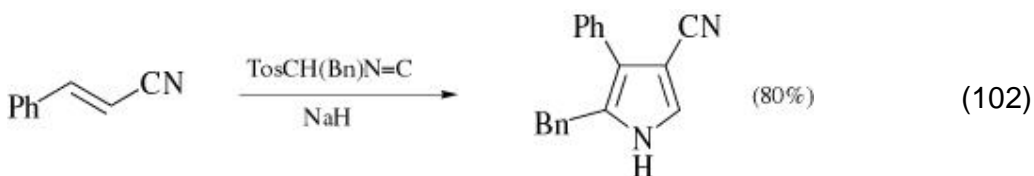
2,3-Dialkenyl-substituted pyrroles are formed when the above reactions are extended to the use of dienic Michael acceptors and alkenyl substituted TosMIC homologs as reactants (Scheme 5). The six- π electron system of these 2,3-dialkenylpyrroles forms the basis of a novel synthesis of indoles through electrocyclic ring closure followed by dehydrogenation. The substituent on the TosMIC homolog thus becomes an integral part of the benzene moiety of the indole skeleton.

8.1. Pyrroles from Michael Acceptors

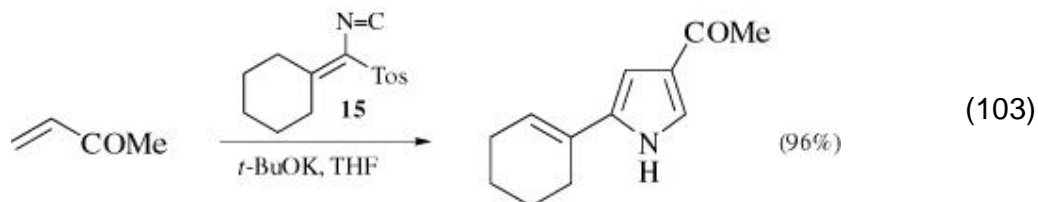
A typical example of the TosMIC-based pyrrole synthesis (Eq. [101](#)) shows that ring positions 1, 2, and 5 remain unsubstituted. ([127](#))



When TosMIC is replaced by a monosubstituted TosMIC homolog, an additional substituent is introduced in position 2 (Eq. [102](#)). ([69](#)) In all cases, the 1 and 5 positions will carry no substituents.



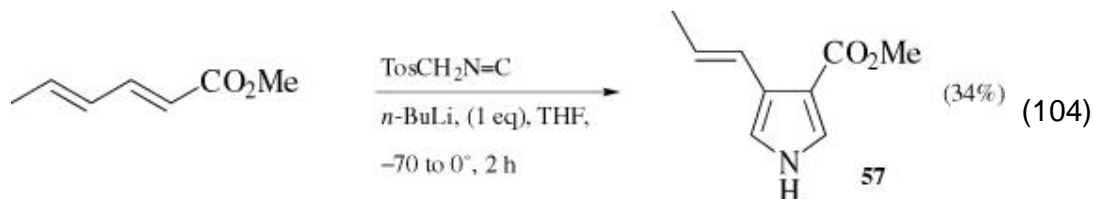
The (formal) condensation product **15** of TosMIC and cyclohexanone gives a 2,4-disubstituted pyrrole (Eq. 103). (128)

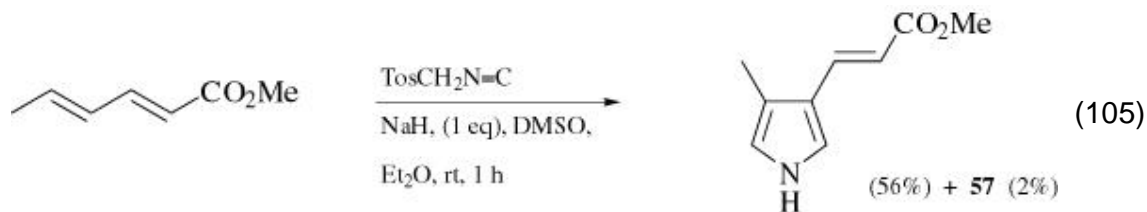


Scheme 6 offers two reasonable mechanisms, [1] and [2], to explain the results of Eqs. 101–103. In mechanism [1], after the key addition and cyclization steps, prototropic shifts followed by a final aromatization through the elimination of toluenesulfinate anion lead to the observed products. In mechanism [2], elimination of sulfinate anion precedes the ring-closing reaction. Compound **56** with $R^1 = R^3 = \text{H}$, $R^2 = \text{CH}_3$, and $\text{EWG} = \text{CO}_2\text{Et}$ is the only intermediate in the pyrrole synthesis of which identification has been claimed, although no details were given. (129)

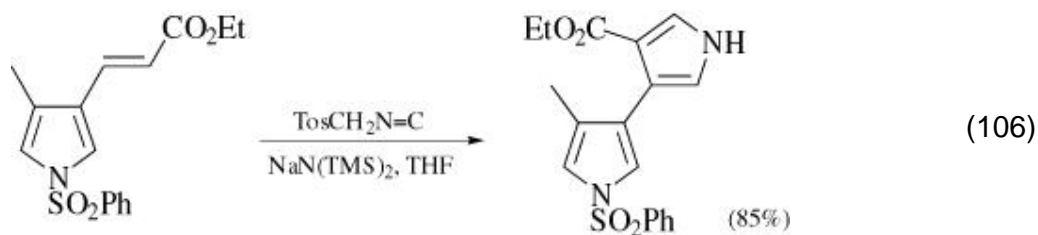
The diverse Michael acceptors **54** used in reactions analogous to Eqs. 101–103 were usually the trans isomers, but cis isomers or cis-trans mixtures have also been employed. (63) In these Michael acceptors, the following electron-withdrawing groups have been used successfully: nitro, aroyl, alkanoyl, alkoxy carbonyl, arylsulfonyl and arylsulfinyl, cyano, carboxamido, and imidoyl. Only the carbox-aldehyde function fails, since these substrates form oxazoles. α , β -Unsaturated aldimines can form both pyrroles and imidazoles, as previously discussed.

With extended Michael acceptors, addition can be directed to the α , β (Eq. 104) or γ , δ (Eq. 105) double bond, according to the reaction conditions. (79, 91)

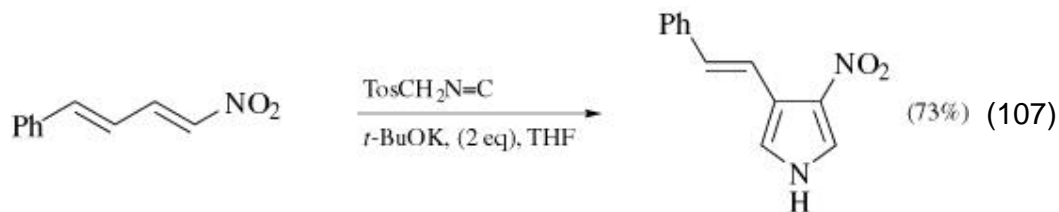




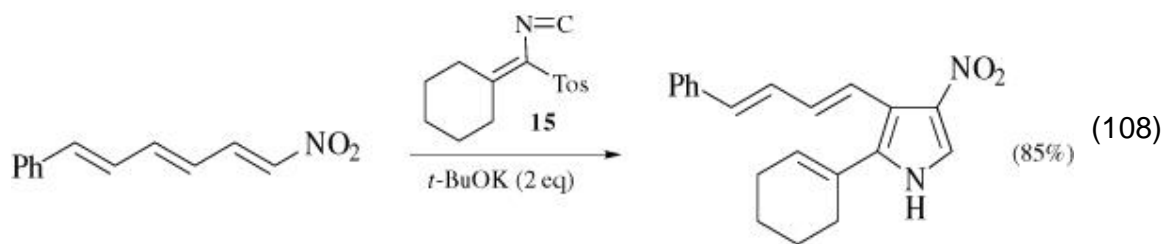
As part of the synthesis of a segment of antitumor agent CC-1065 the reaction of Eq. 105 was extended to the formation of a 3, 3'-bipyrrole (Eq. 106). (91, 129) Tripenta-, and heptapyrroles have been prepared in a comparable fashion. (130)



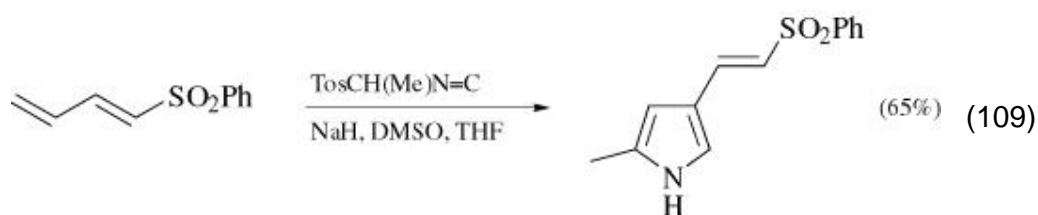
With 1-nitro-4-phenyl-1,3-butadiene, only one pyrrole is formed (Eq. 107). Variation of the base/solvent system did not lead to a pyrrole derived from the γ , δ double bond in this case. (131)



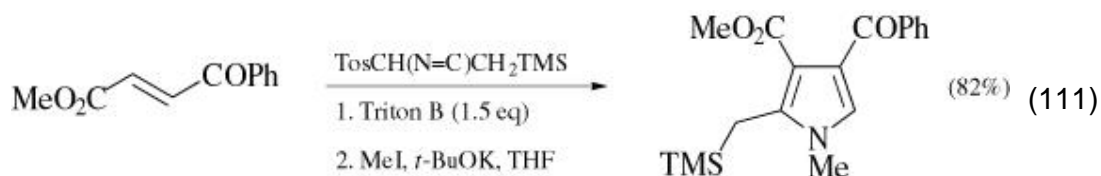
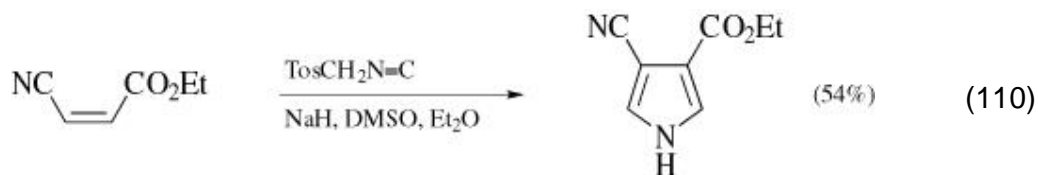
1-Nitro-6-phenyl-1,3,5-hexatriene behaves correspondingly in the reaction with the TosMIC homolog 15, affording a single pyrrole by addition to the α , β double bond (Eq. 108). (131)



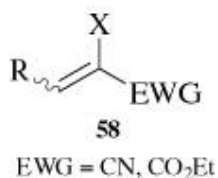
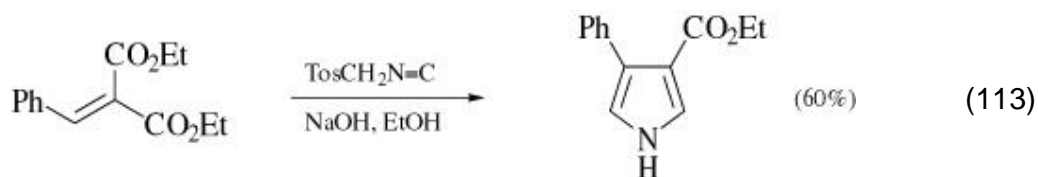
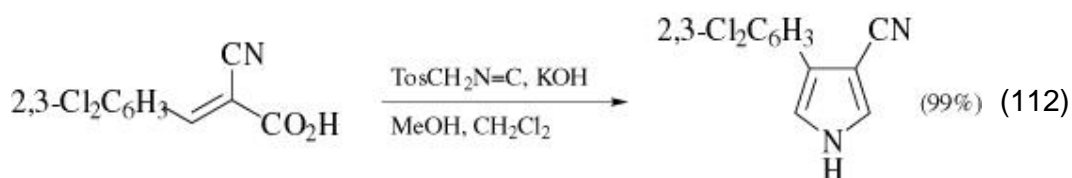
1-(Phenylsulfonyl)-1,3-butadiene reacts with 1-tosylethyl isocyanide exclusively at the γ , δ double bond. (132, 133)



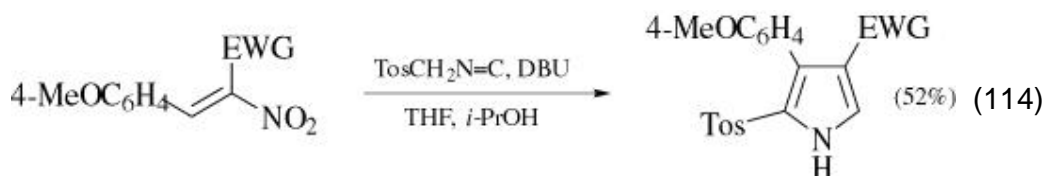
Further variation of the Michael acceptor molecule 54, beyond R = alkyl, alkenyl, or aryl, is possible: pyrroles are also formed when R represents a second electron-withdrawing group. With two different electron-withdrawing groups, the reaction with TosMIC affords a single pyrrole (Eq. 110) (134) and with a TosMIC homolog, similar reactions can also be regioselective. The direction of this process is governed by the more strongly electron-withdrawing substituent (Eq. 111). (63, 93)



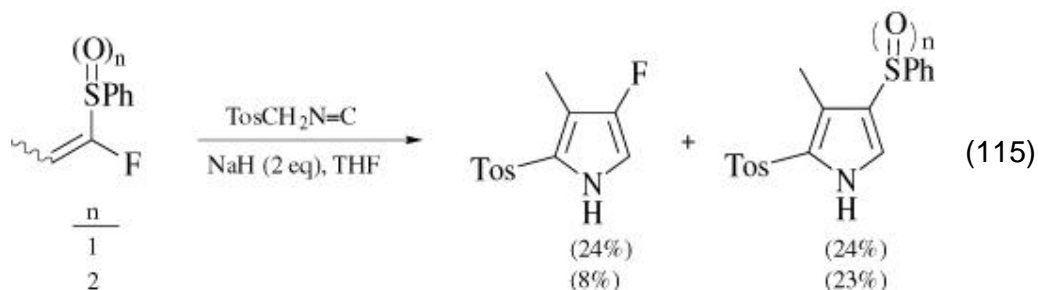
All examples discussed above involve reactions of TosMIC (or TosMIC homologs) with Michael acceptors carrying at least one hydrogen at each of the two sp^2 carbon atoms that will become part of the pyrrole ring. This, however, is not a necessary condition. Sometimes, it is advantageous to increase the Michael acceptor reactivity by using two electron-withdrawing groups at the same carbon atom, as in Eqs. 112 (135) and 113. (136) Obviously, to form a pyrrole one of these groups has to be removed in the course of the reaction. This was shown to be possible for $X = \text{CO}_2\text{H}$, CO_2R , and CONH_2 (in 58). (135-137)



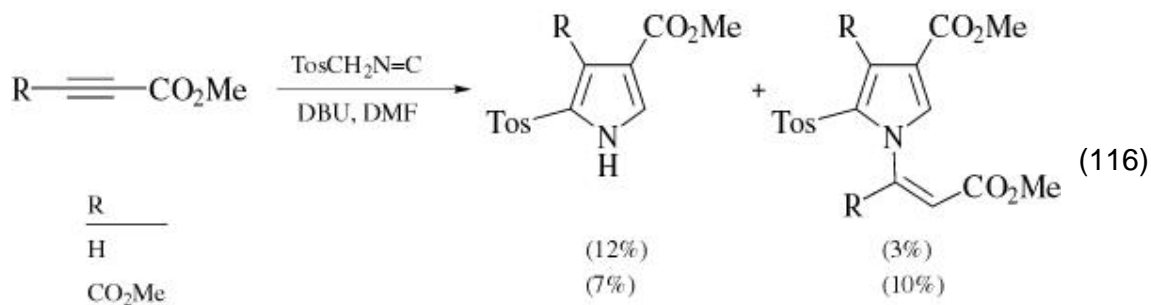
In a related process that uses 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the nitro group is both the activating group and the leaving group. (138)



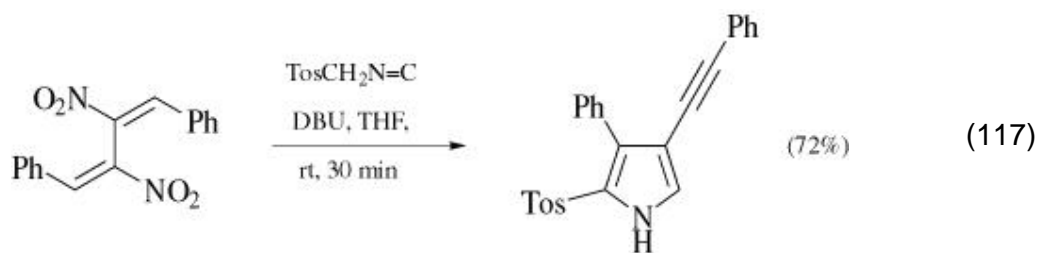
Eq. 115 (139) shows that two different electron-withdrawing groups at the same carbon may compete as leaving groups, in contrast to Eq. 112.



Few examples have been reported of pyrroles prepared from TosMIC and Michael acceptors with a C – C triple bond. Such reactions give 2-tosylpyrroles (Eq. 116). (140)



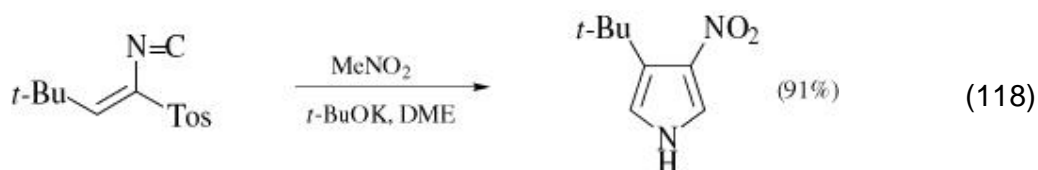
In a final example, two nitro groups are eliminated: one to form a pyrrole and one to form a triple bond (Eq. 117). (141)



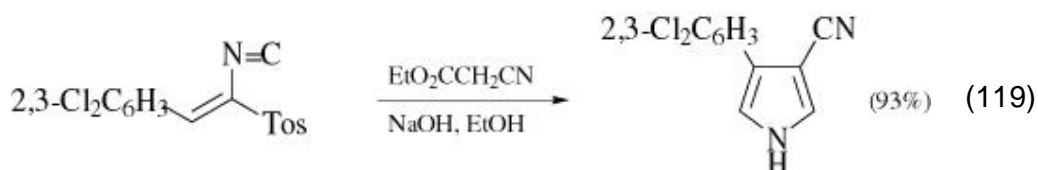
It is also possible to prepare 2,3,4-trisubstituted pyrroles using (formal) TosMIC derivatives that carry a substituent together with a leaving group at the "isocyano" carbon. The use of such synthons $\text{TosCH}_2\text{N}=\text{C}(\text{XCH}_3)\text{R}$ ($\text{X} = \text{O}, \text{S}$) for the synthesis of pyrroles (47-51) is not covered in detail in this chapter.

8.2. Pyrroles from 1-Isocyano-1-tosyl-1-alkenes

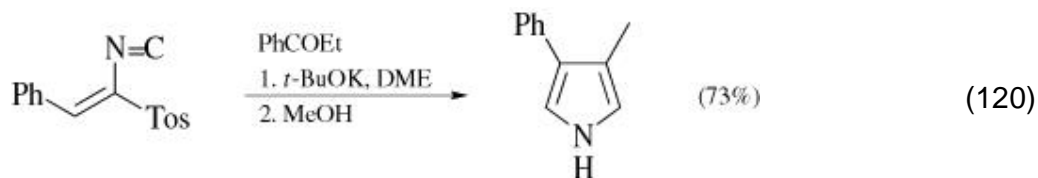
Being Michael acceptors, 1-isocyano-1-tosyl-1-alkenes **55** are susceptible to reaction with nucleophiles at the β carbon. This, in combination with the electrophilic nature of the isocyano carbon, provides an efficient synthesis of 3-nitropyrroles (Eq. 118). (136, 142)



Extension of the method of Eq. 118 to synthesize pyrroles with substituents at C3 other than the nitro group is possible. Replacement of the 3-nitro function by the following groups has been realized: cyano, carboxylate, acetyl, benzoyl, and even methyl and phenyl. (136) It is, however, not possible to prepare a cyanopyrrole simply by replacing nitromethane (in Eq. 118) by acetonitrile. The CH acidity of acetonitrile needs to be enhanced by an acidifying auxiliary, for example, by using ethyl cyanoacetate (Eq. 119). (136) As before, the reaction is carried out in one operation; the auxiliary is removed by nucleophilic attack of ethoxide (Scheme 7).

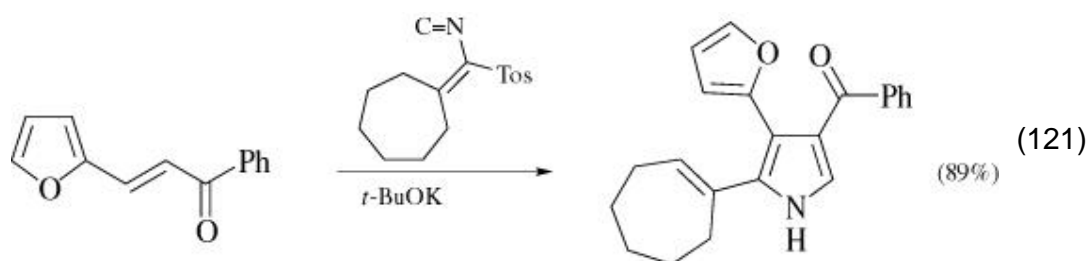


3-Acetyl-4-phenylpyrrole is similarly obtained from acetylacetone. (136) The method also allows the introduction of substituents at C3 that are not of the electron-withdrawing type (Eq. 120). (136)



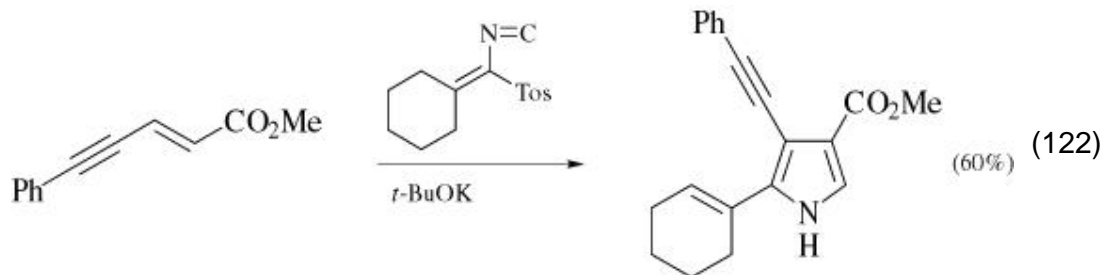
8.3. 2,3-Dialkenylpyrroles and Indoles

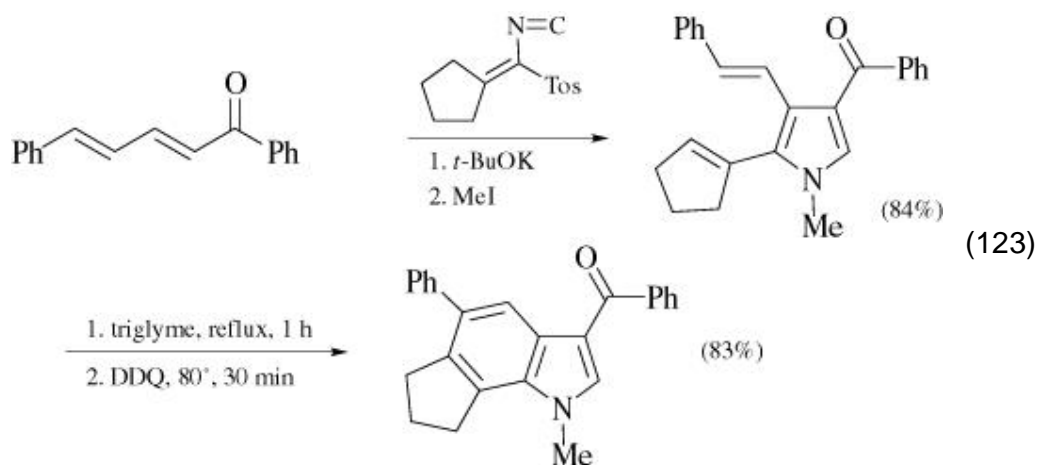
Reactions of the extended anions derived from alkylidene TosMIC derivatives with Michael acceptors provide an efficient synthesis of 2,3-(dialk-1-enyl) pyrroles, as in Eq. 121. (128)



For obvious reasons the pyrrole ring in Eq. 121 is formed exclusively at the α , β double bond of the substrate molecule. The same is true for the reaction of the conjugated enyne acceptor of Eq. 122, which reflects reduced reactivity of the triple bond relative to the double bond. (63, 143) Such products are nicely set up for six π electron cyclizations to form indoles. Eq. 123 gives an example of a thermal electrocyclic ring closure, followed by dehydrogenation with the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). (128)

This method of synthesizing indoles is rather unusual in that the benzene ring is built onto a preformed pyrrole, (128) instead of the other way around. (144, 145) The cyclization step may be carried out thermally (63, 80, 128, 131, 146) or photochemically. (128, 143)



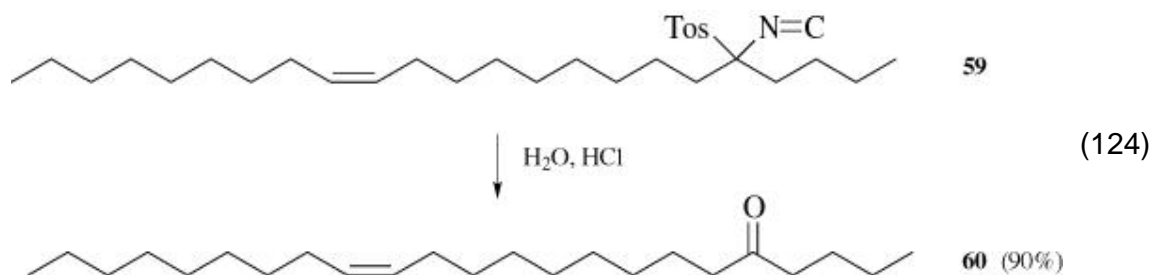


Benzoxazoles and benzimidazoles are accessible similarly by electrocyclization and dehydrogenation of 2,3-(dialk-1-enyl)-oxazoles and -imidazoles, respectively. There is, however, only one brief report of this process, containing a limited number of examples. (80)

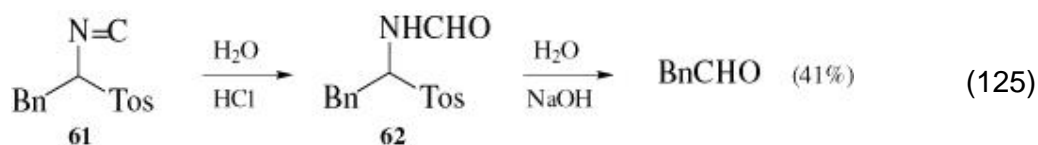
9. Synthesis of Ketones by Hydrolysis of TosMIC

Derivatives

Hydrolysis of TosMIC and similar compounds by acid ultimately produces aldehydes or ketones via initial hydration of the isocyanide. Eq. 124 provides an example. Compound **59**, obtained by a twofold alkylation of TosMIC, is hydrolyzed to ketone **60**. (107) This protocol shows TosMIC as a CO connective reagent. Wolff-Kishner reduction of ketone **60** gives muscalure. The application of TosMIC as a CO and CH₂ connective reagent is comparable to the use of other compounds with an activated methylene group, such as 1,3-dithiane (146a) and methylthiomethyl 4-tolyl sulfone. (147)

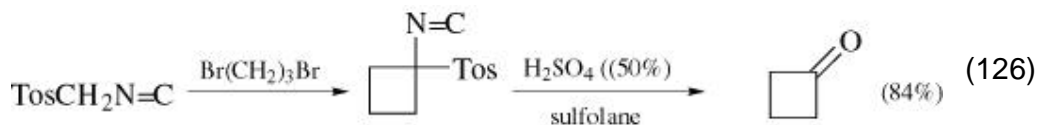


This methodology is not restricted to the synthesis of monofunctional ketones. The same principles apply to the synthesis of enones, α -hydroxy ketones and aldehydes, 1,2-, 1,4-, 1,5-, and higher diketones, triketones, and tetraketones. Some specific examples of the TosMIC ketone synthesis are found in previous sections (Eqs. 13, 33, 34, 56, 70, 71, and 76–79). Strikingly, only one aldehyde has been prepared by hydrolysis of a monosubstituted TosMIC derivative (apart from the synthesis of α -hydroxy aldehydes according to Eq. 143). Phenylacetaldehyde is obtained by acid hydration of 2-phenyl-1-tosylethyl isocyanide (**61**), and subsequent treatment of formamide **62** with aqueous base (Eq. 125). (73)

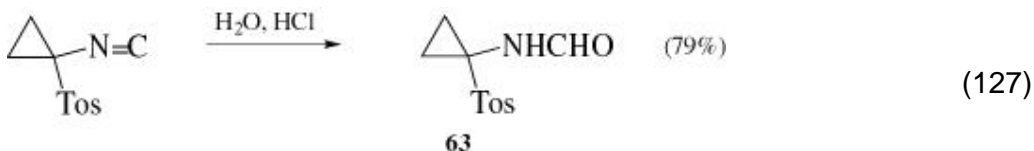


9.1. Ketones

Cycloalkylation of TosMIC is possible with dihaloalkanes such as 1,3-dibromopropane. This transformation forms the basis for an efficient synthesis of cyclobutanone. (148)



The same approach leads to the synthesis of optically active 2-methylcyclobutanone, both from (*S*)-(+)-1,3-dibromobutane and TosMIC and from (\pm)-1,3-dibromobutane and (+)-neomenthylsulfonylmethyl isocyanide. (39) Other cyclic ketones have been synthesized by the same method, including examples of a 10-membered (149) and an 18-membered ring. (150) As previously noted, acid hydrolysis of the 3-membered ring compound prepared from TosMIC and 1,2-dibromoethane (73, 99) gives formamide **63** and not cyclopropanone. (99)

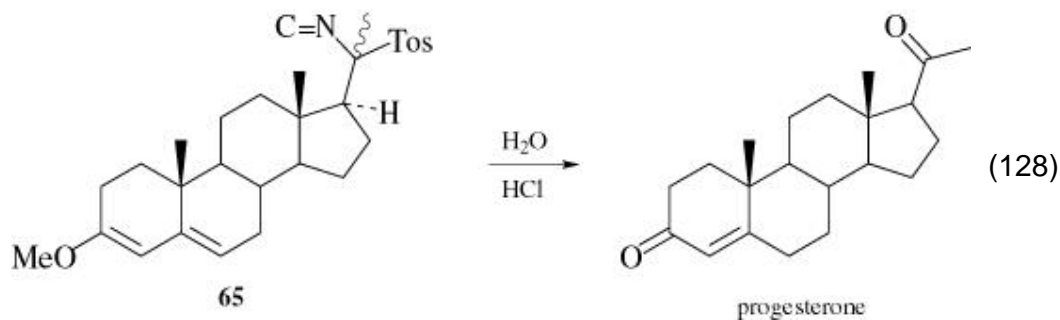


The considerable difference in stability between the various types of geminal tosyl formamido compounds is understandable on the basis of the structure of the formyliminium species **64** formed upon spontaneous or acid-promoted ionization. Dialkyl substitution stabilises the carbocation to the point where the intermediates are not isolable, with the exception of the cyclopropyl case, where carbocation formation is disfavored.

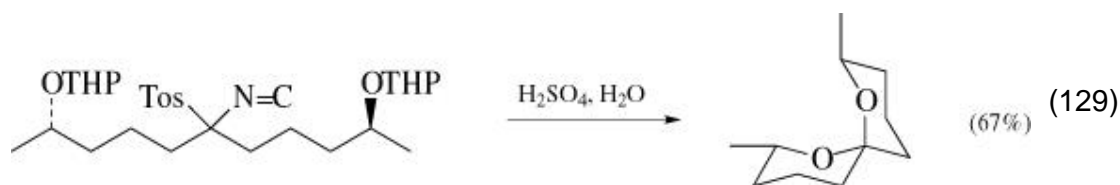


The synthesis of progesterone from a 17-ketosteroid illustrates several aspects of TosMIC chemistry. (45) A condensation-dehydration sequence on

the 17-keto 3,5-dienol ether is followed by reduction and alkylation to afford **65**; subsequent acid hydrolysis (Eq. 128) in the usual way gives progesterone in excellent overall yield.

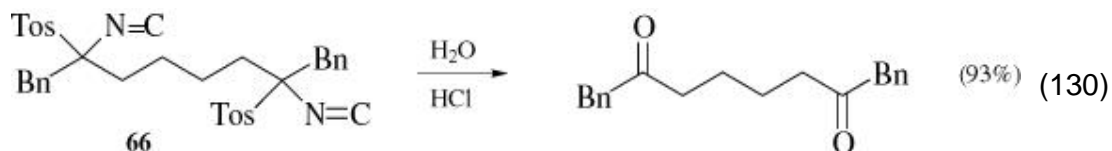


This ketone synthesis has been used for the synthesis of chiral spiroketals, combining the hydrolysis and ketalization steps (olive fruit fly pheromones, Eq. 129). (151)



9.2. Diketones

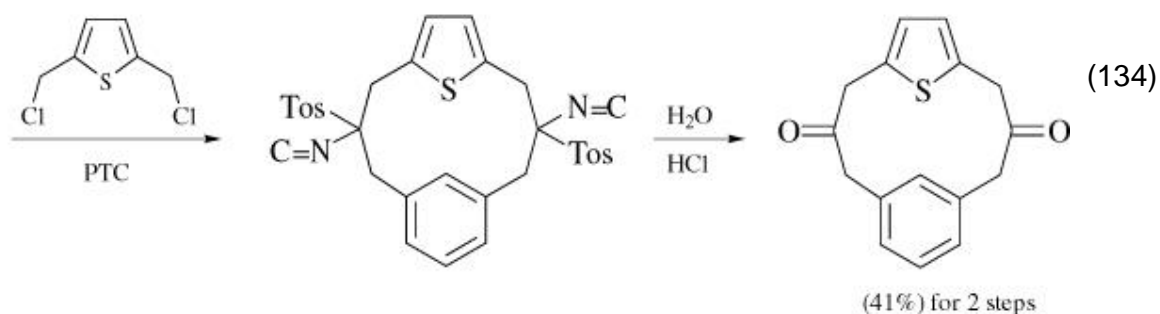
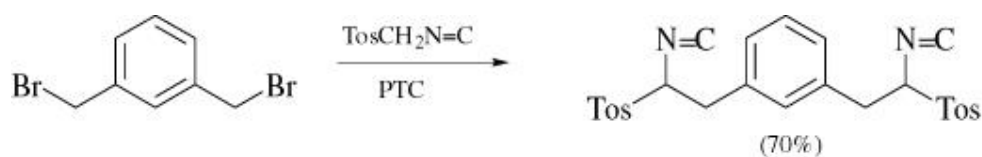
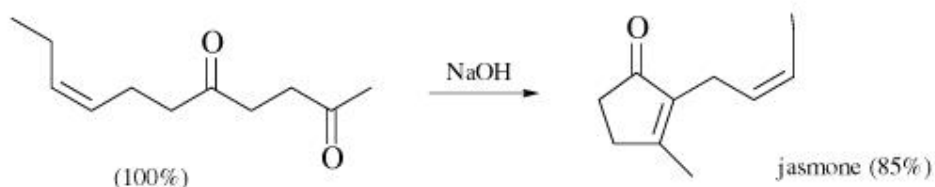
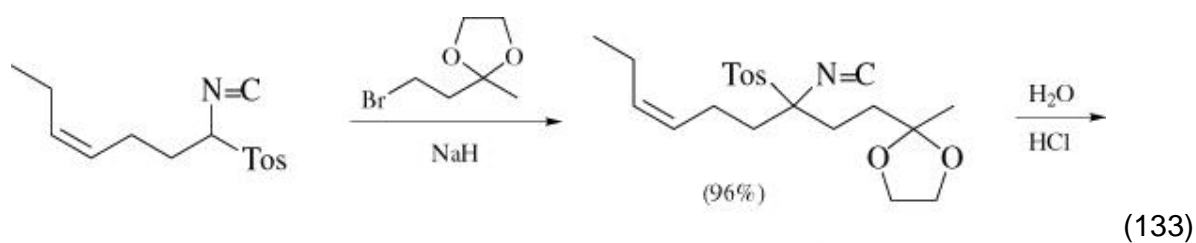
Acid-promoted hydrolysis of products such as **66**, obtained from 1,*n*-dihaloalkanes and 2 equivalents of a monosubstituted TosMIC derivative, provides symmetrical 1,*(n + 2)*-diketones (Eq. 130). A related stepwise alkylation protocol leads to unsymmetrical diketones (Eq. 131). (100)



Many symmetric as well as unsymmetric cyclic diketones, particularly in the cyclophane class, are available by a simple extension of this chemistry. Two molecules of TosMIC are first interconnected with a 1,n-dihalo compound in a double monoalkylation step. Reaction with a second dihalo compound, followed by acid hydrolysis, leads to the cyclic diketone (Eq. 134). (92, 153)

9.3. Tri- and Tetraketones

Eq. 76 and 77 already showed that extrapolation of the principles of Eq. 132 can produce cyclic tri- and tetraketones.



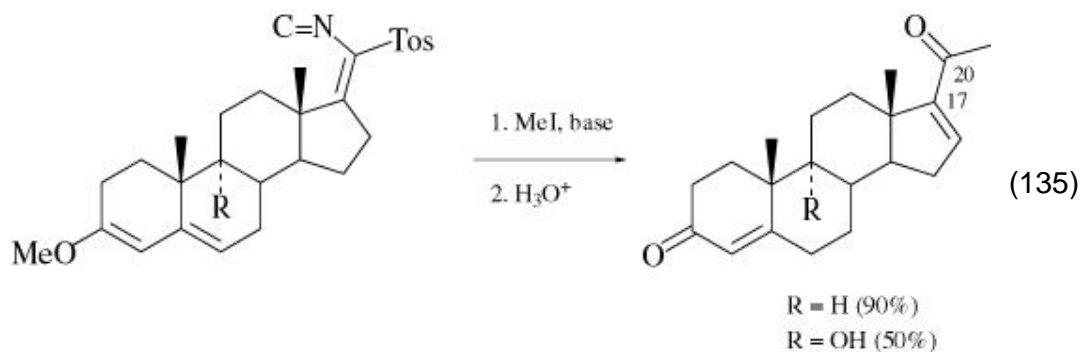
Another interesting example is the threefold use of TosMIC as a CO connective reagent between two molecules of

1,3,5-tri(4-bromomethylphenyl)benzene. (154)

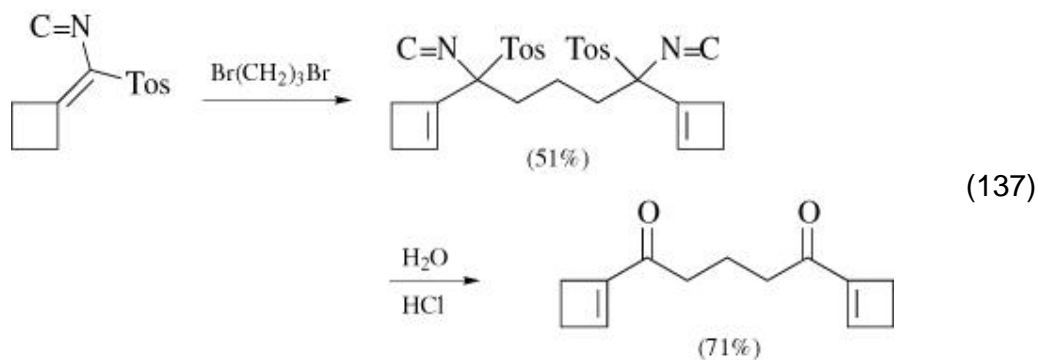
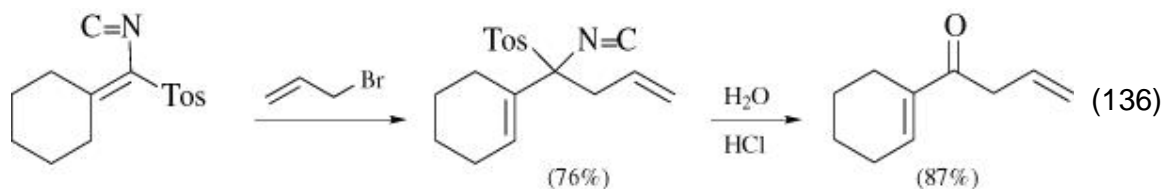
Cyclic tetraketones have been obtained as minor products in reactions that also form di- and triketones. (109, 153, 155, 157)

9.4. Enones

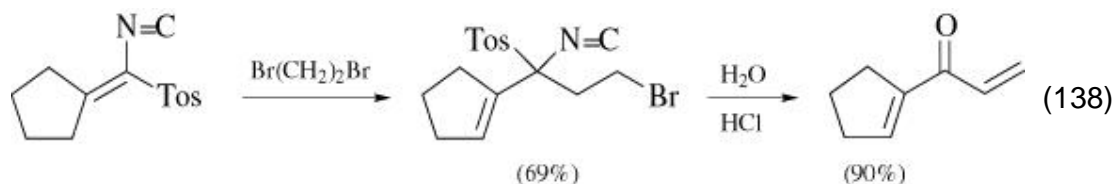
Alkylation of 1-isocyano-1-tosyl-1-alkenes followed by acid hydrolysis affords enones. This method has been used extensively for the introduction of C17 side chains in steroids, as in Eq. 135. (101)



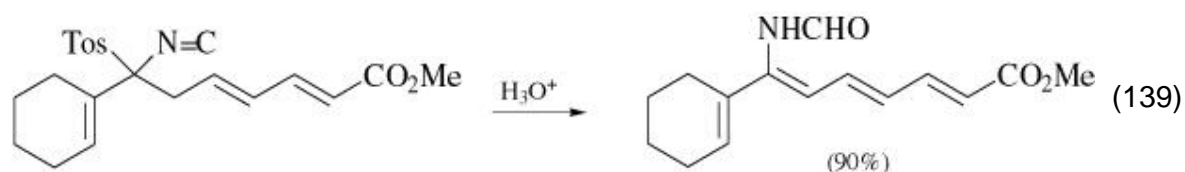
This route can also be used to synthesize nonconjugated olefins and bis(enones) (Eqs. 136 and 137). (101, 103)



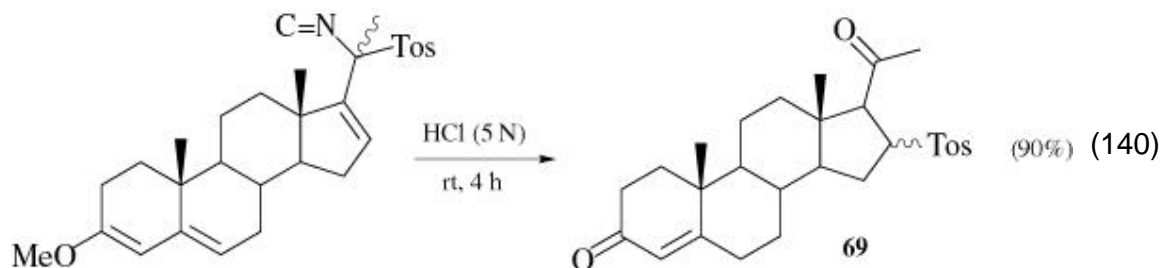
When allyl bromide is replaced by α -bromoacetophenone or ethyl α -bromoacetate, the alkylation step succeeds, but the derived 1,3-diketone and β -keto ester decompose under the acid hydrolysis conditions. (103) α -Halo enones may be obtained using dibromomethane, (101) but the attempted synthesis of a β -bromo enone led to a divinyl ketone (Eq. 138). (103)



The formation of a stable, conjugated enamide in the hydrolysis step has been reported (Eq. 139). (103)

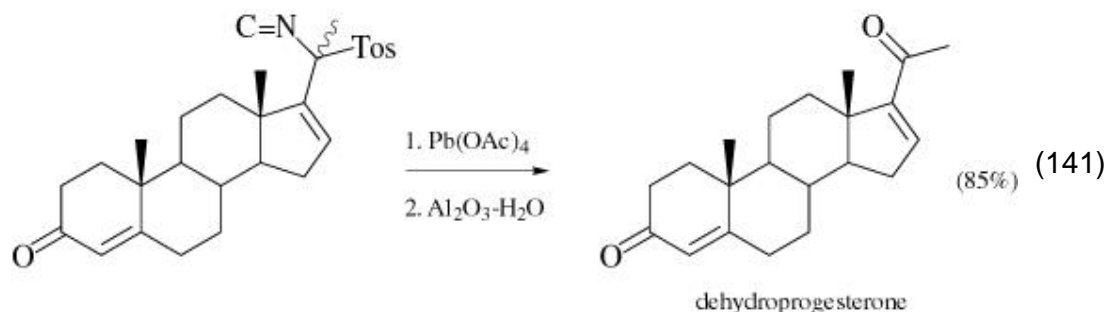


Occasionally, the 4-toluenesulfinic acid formed in the acid hydrolysis step adds to the α , β double bond of the target enone, as exemplified by the formation of the sulfone **69** in high yield during an attempted synthesis of 16-dehydroprogesterone (Eq. 140). (101, 158) When the reaction time was reduced to 30 minutes,



16-dehydroprogesterone is obtained in 75% yield. Further improvement to 90% was obtained by carrying out the hydrolysis in a mixture of dichloromethane and diethyl ether for 3 minutes with 40% aqueous perchloric acid. (101)

Alternatively, the isocyanide can first be oxidized with lead tetraacetate to an isocyanate, which is hydrolyzed on alumina (Eq. 141). To prevent oxidation in the A/B ring moiety, the dienol protecting group must be removed prior to the oxidative step. (101) A similar oxidative hydrolysis to form a saturated ketone, using peracetic acid or mercury(II) nitrate, has also been reported. (96)

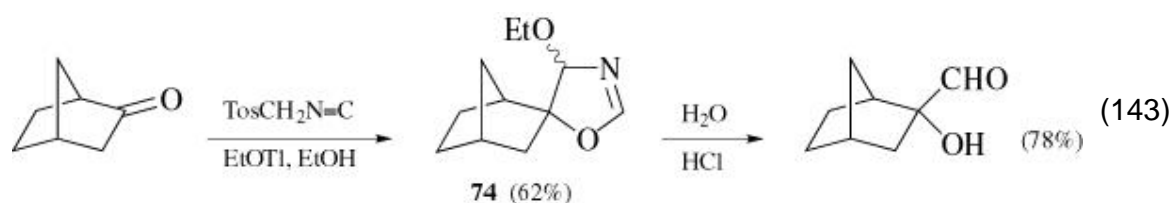
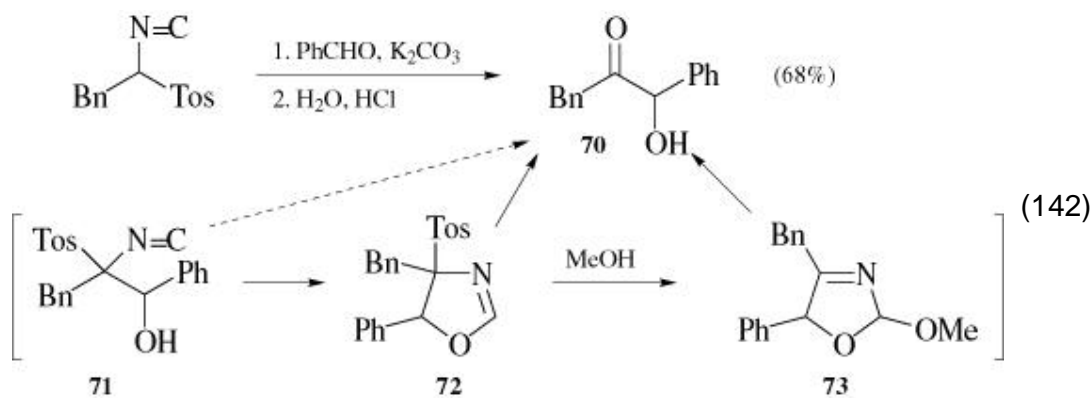


9.5. α -Hydroxy Ketones and α -Hydroxy Aldehydes

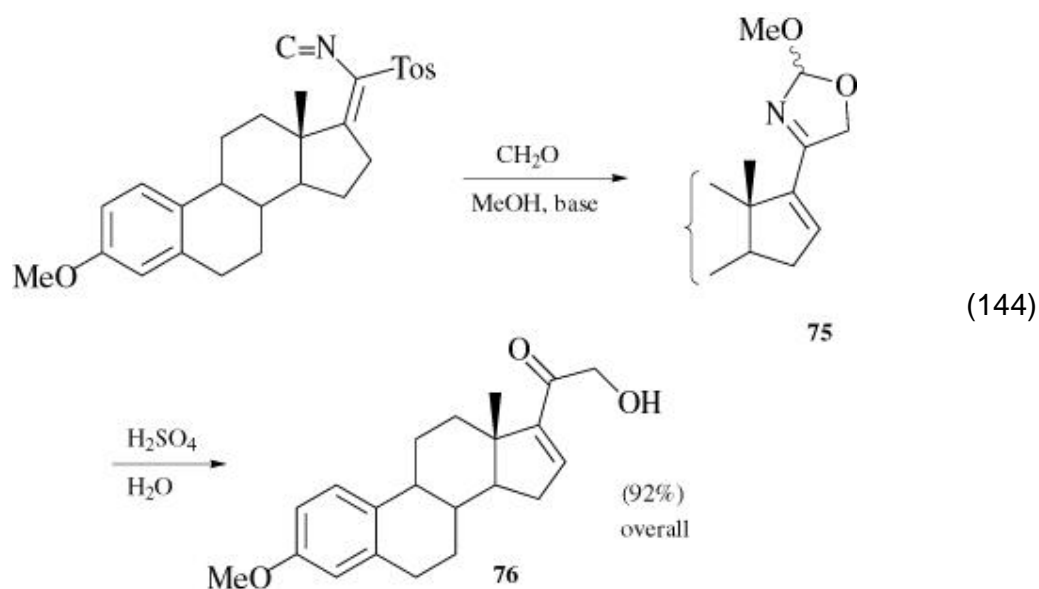
Benzaldehyde and 2-phenyl-1-tosylethyl isocyanide have been made to react in a one-pot process to give 1,3-diphenyl-1-hydroxy-2-propanone (70) (Eq. 142). First, the two reactants are stirred in dry methanol with a catalytic amount of potassium carbonate for 5 minutes at 30°, then for another 5 minutes at 0° after addition of some concentrated hydrochloric acid. (73)

The course of the reaction of Eq. 142 is explained by a base-induced addition of 2-phenyl-1-tosylethyl isocyanide to benzaldehyde to give the (transient) (14) β -hydroxy isocyanide 71. A fast intramolecular α -addition of the hydroxy group to the isocyanato carbon gives 4-tosyloxazoline 72, which by a base-induced addition-elimination process may give the 2-methoxyoxazoline 73. Acid hydrolysis of any of these potential intermediates would lead to the hydroxy ketone 70.

The reaction of TosMIC with ketones in alcoholic solvents, followed by hydrolysis, leads to α -hydroxy aldehydes (Eq. 143). Using thallium ethoxide as the base, the oxazoline 74 has been isolated and characterized. Hydrolysis with dilute hydrochloric acid in tetrahydrofuran at room temperature gives mostly the monomeric α -hydroxy aldehyde. (72)



The most prominent application of the α -hydroxy ketone synthesis, for the introduction of the corticoidal 17-hydroxyacetyl side chain in 17-ketosteroids, makes use of paraformaldehyde (Eq. 144). (70, 159) The 2-methoxyoxazoline **75** may be isolated prior to acid hydrolysis to 21-hydroxy-3-methoxy-19-norpregna-1,3,5(10),16-tetraen-20-one (**76**). (70)



Partial hydrolysis of 2-methoxyoxazolines such as **75** with 60% formic acid leads directly to 17-(formyloxy) acetyl side chains. The formyl protection allows the bis-hydroxylation of the C16-C17 double bond with potassium permanganate. This is a crucial step in a practical synthesis of the anti-inflammatory drug, triamcinolone acetonide (Eq. **13**). (**159**)

10. Reduction of TosMIC Derivatives

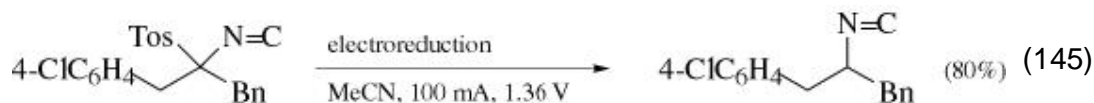
Under appropriate conditions, the reduction of TosMIC derivatives may be controlled so as to produce alkanes, isocyanides, and methylamine derivatives.

10.1. Alkanes

The complete reductive removal of both the tosyl and the isocyno groups to give a methylene group, which was exemplified earlier in Eqs. 73–75, is rationalized in Scheme 8. (105) One-electron transfer, followed by loss of lithium cyanide from the radical anion 77 gives the radical 78, which is further reduced and protonated to form the sulfone 79. This sulfone is reduced in situ in a known process (159a) to the final product. Sulfone 79 has been identified as a possible intermediate upon use of an insufficient amount of lithium. (105) Isolated C – C double and triple bonds, ether, and acetal functions are unaffected, (105) but partial conversion of ester groups into amides requires an in situ reesterification step. (160)

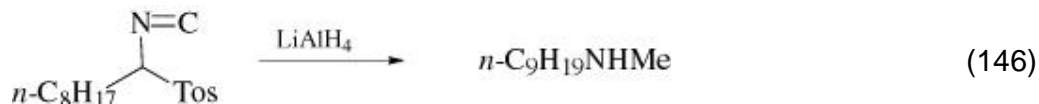
10.2. Alkyl and Aralkyl Isocyanides

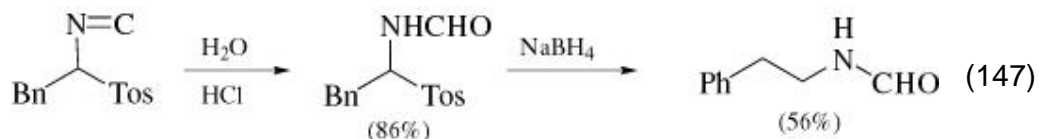
When the reduction of mono- and disubstituted derivatives of TosMIC is carried out by electrochemical means, only the sulfonyl group is removed (Eq. 145). This electroreductive detosylation, which is reported to proceed via a two-electron transfer process, has been used to prepare a number of symmetrical and unsymmetrical alkyl and aralkyl isocyanides. (161)



10.3. *N*-Methylamines

Mono- and disubstituted TosMIC derivatives are reduced to *N*-methylamines by lithium aluminum hydride (Eq. 146); this reduction is assumed to take place

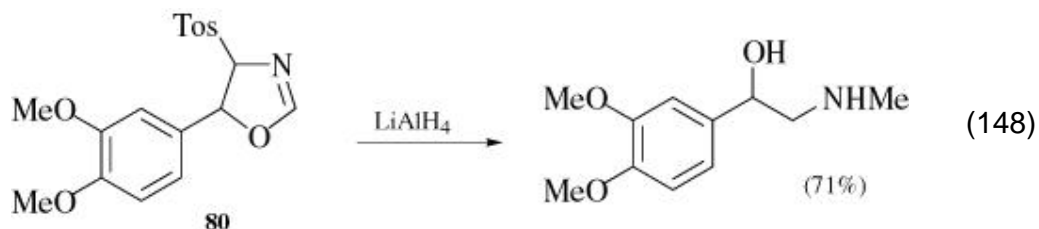




via *N*-methylamines. (73) Sodium borohydride cannot be used, although this reagent will detosylate the acid hydration product of 2-phenyl-1-tosylethyl isocyanide. This is the only reported example of this type of reaction. (73)

10.4. β -Hydroxy *N*-methylamines

β -Hydroxy *N*-methylamines are obtained from 4-tosyloxazolines such as **80** by reductive ring opening with lithium aluminum hydride (Eq. 148). The 4-tosyloxazolines are usually reduced without purification. (73)



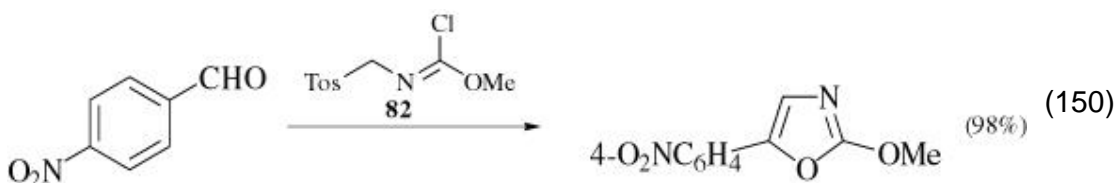
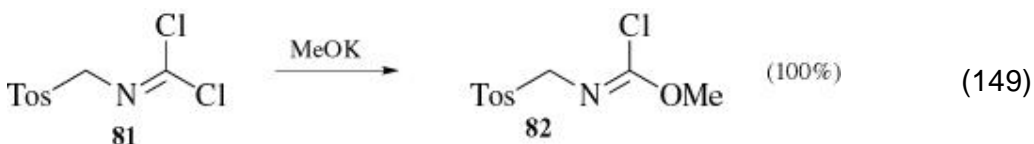
So far, this conversion has been carried out only with TosMIC, not with TosMIC homologs. Optically active β -hydroxy *N*-methylamines are obtained from optically active 4-tosyloxazolines, as was shown previously in Eqs. 35 and 37. (74, 75)

11. Miscellaneous

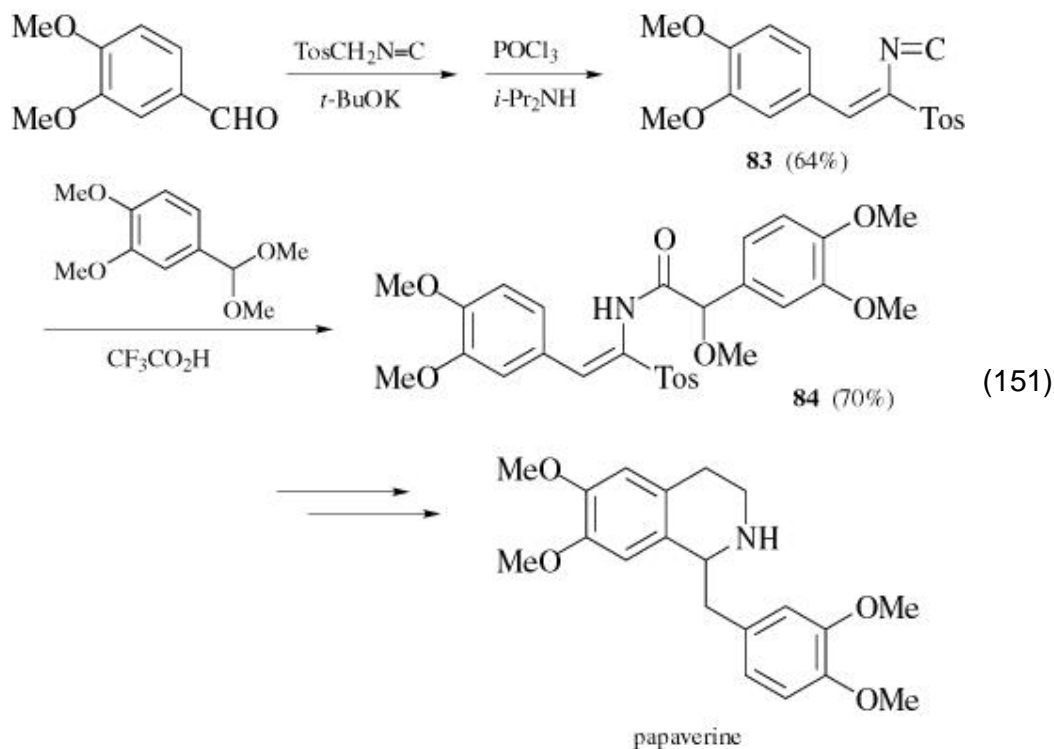
Since the following reactions are not main stream synthetic uses of TosMIC, they are treated in an exemplary way only. For details the reader is referred to the references given in the text and Tables.

11.1. α -Additions to the Isocyano Carbon of TosMIC

Several reactions of TosMIC are known in which the tosylmethyl group remains unchanged, notably α -additions to the isocyano carbon. For example, TosMIC reacts with dry gaseous chlorine to give an isolable solid α -adduct **81**. (47, 51) Replacement of one of the chlorines by methoxy provides the reagent **82** (Eq. 149), which has been used for the synthesis of azoles bearing a substituent at C2. Eq. 150 gives one example (52) of this type of reaction. (46-51, 162)



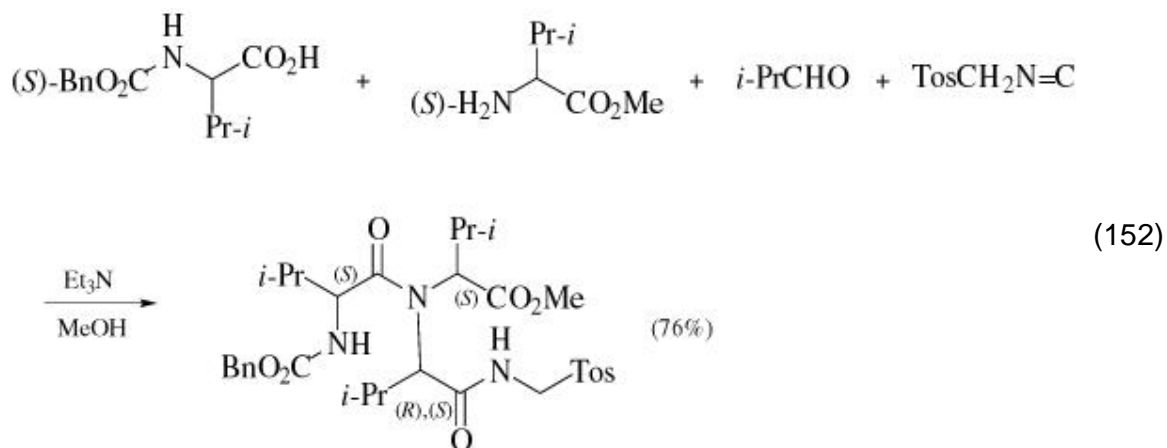
α -Additions of acid chlorides, anhydrides, and 1-hydroxy-2-thiopyridinone esters to TosMIC are also known. (163-166) The (formal) condensation product **83** of TosMIC and veratraldehyde has been reacted with veratraldehyde acetal to give amide **84**, which was further transformed to papaverine. (95)



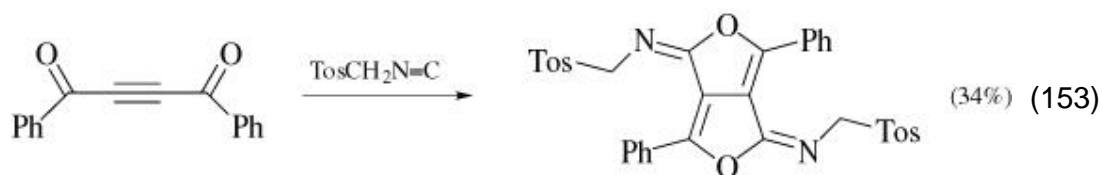
TosMIC has been used as the isocyno component in a large series of Ugi four-component reactions (12, 167) to form α -amino acid derivatives, using α -amino esters as the amine component, benzyloxycarbonyl-protected α -amino acids as the acidic component, and isobutyraldehyde. (168) The example of Eq. 152 shows that this route to dipeptide derivatives is not hampered by the presence of three bulky isopropyl groups.

11.2. Cycloadditions to the Isocyno Carbon of TosMIC

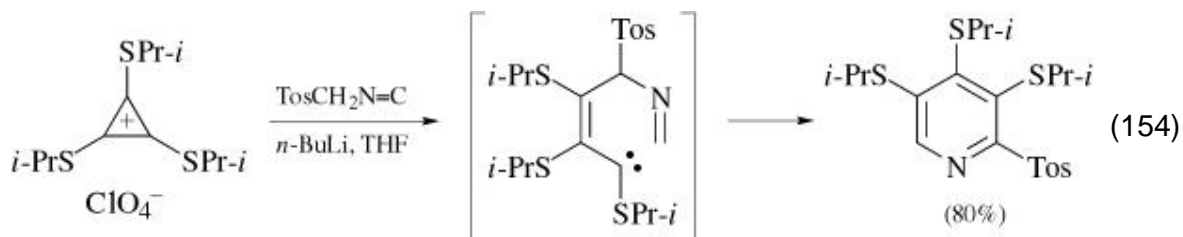
These reactions which form heterocyclic compounds by incorporation of the TosMIC isocyno carbon into a ring are essentially α -additions. They are, however, listed separately from the foregoing reactions, in view of the different product structures. Cycloadducts have been obtained from TosMIC by reactions with ketenes, (169) with dibenzoyldiazomethane, (170) and with a ketene *N,N*-acetal. (171)



Under neutral conditions dibenzoylacetylene reacts with two molecules of TosMIC according to Eq. 153. (172)



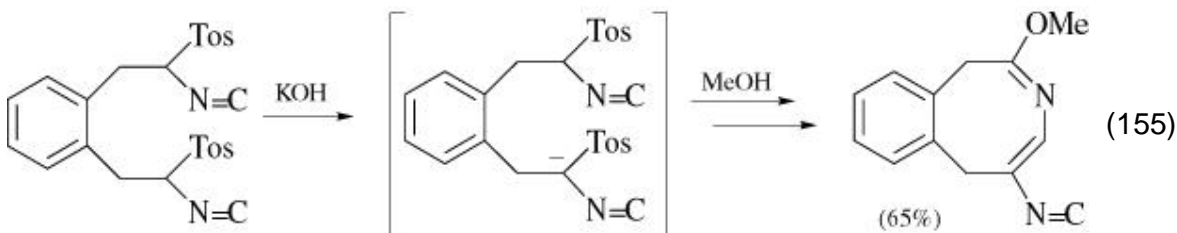
Various 3-membered ring compounds react in different ways with TosMIC. (173-176) Eq. 154 gives an example; (176) it is the only report of the formation of a pyridine ring with the use of TosMIC. The reaction is assumed to proceed via a vinylcarbene.



A carbene-chromium complex has been used to form a ketenimine intermediate, which by a zinc chloride catalyzed cyclization gives a naphthalene derivative, (177) and a zirconacyclopentane intermediate has

been used to convert a geminal diallyl compound into a cyclopentanone derivative via insertion of TosMIC into the zirconium complex. (178)

An 8-membered ring is formed by a base-induced intramolecular cyclization of the reaction product of 1,2-(dibromomethyl)benzene and two molecules of TosMIC (Eq. 155). (82)

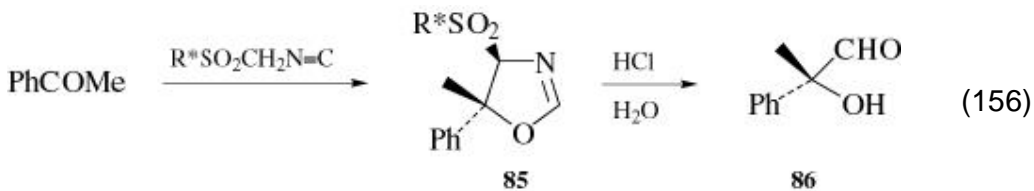


11.3. TosMIC as a Metal Ligand

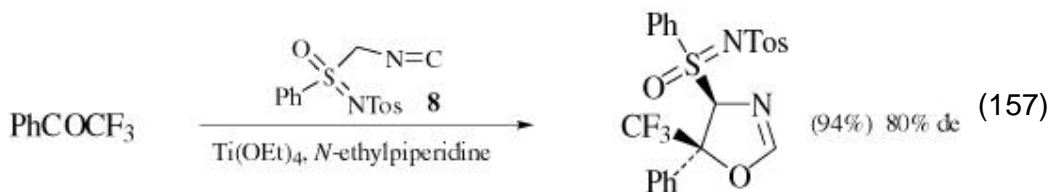
TosMIC forms stable, isolable complexes with various metal compounds. In these complexes, TosMIC coordinates with the metal through the isocyano carbon, as do many other isocyanides. (10) In certain copper complexes, the sulfonyl oxygens also appear to be involved in the coordination. (179)

11.4. Analogs of TosMIC

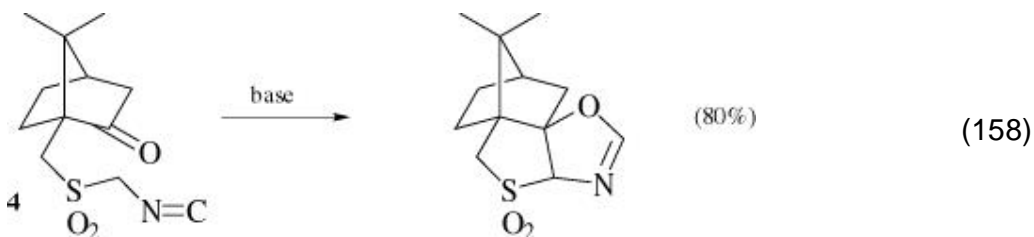
Synthetic applications of TosMIC analogs are limited in comparison with the parent compound. Two items are worthy of note: chiral analogs, and methylsulfonyl isocyanide. Of the chiral TosMIC analogs (2–8, 11), two have been prepared in an enantiomerically pure state (3 and 4). (40) Four isocyanomethylsulfonamides 9 to 12 are known; of these, the chiral proline derivative 11 was obtained as an impure oil only. (180) The scope of application of these chiral TosMIC analogs 2 to 8 has remained somewhat limited, since asymmetric inductions obtained with these synthons are modest. Reactions of isocyanides 2, 3, and 5, 6, 7 with acetophenone, as in Eq. 156, gave oxazolines 85 in diastereomeric excess ranging from 7 to 40%, and eventually α -hydroxy aldehydes 86 in enantiomeric excesses of 16 to 31%. (40)



Better results were obtained with sulfonylmethyl isocyanide **8**, which, however, requires a more reactive substrate such as trifluoroacetophenone (Eq. 157). (40)

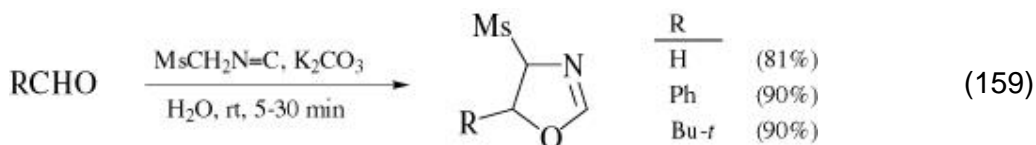


Sulfonylmethyl isocyanide **4**, derived from (+)-10-camphorsulfonic acid, has the disadvantage of internal cyclization (Eq. 158) when the substrate molecule in an intermolecular process is not sufficiently reactive. (40, 180)

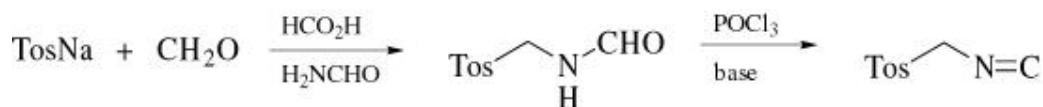


The application of neomenthylsulfonylmethyl isocyanide (**2**) to the synthesis of 2-methylcyclobutanone in high optical purity (cf. Eq. 130) is based on the separation of diastereomers, not on asymmetric induction. (39)

Methylsulfonylmethyl isocyanide (30, 54, 181) (MesMIC) deserves to be further investigated for two reasons. Firstly, the “atom efficiency” of MesMIC in reactions is superior to TosMIC when the loss of methanesulfinic acid (molecular weight 80) is compared to 4-toluenesulfinic acid (molecular weight 156). Secondly, the significant solubility of MesMIC in water (10 g in 100 mL) offers the possibility of performing TosMIC-type reactions in aqueous solution. Only a few such reactions have been investigated, for example those of Eq. 159. (94)

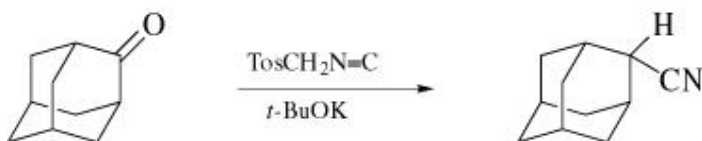


12. Experimental Procedures



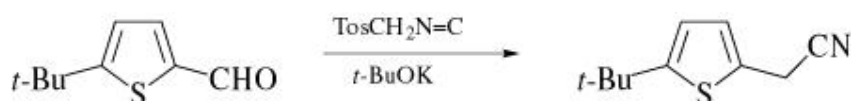
12.1.1. *N*-(4-Tolylsulfonylmethyl) formamide (30) and 4-tolylsulfonylmethyl isocyanide (Two-step Synthesis of TosMIC, Eq. 16) (31, 42)

A mixture of anhydrous sodium 4-toluenesulfinate (18.35 g, 100 mmol), formamide (30 mL, 750 mmol), paraformaldehyde (12.0 g, 400 mmol), and formic acid (19 mL, 700 mmol) was heated at 90° for 2 hours. The clear solution was cooled to room temperature and water (75 mL) was added. The mixture was stored in a refrigerator overnight. The solid was collected, washed with five 10-mL portions of icewater, then dried in vacuum over calcium chloride at 60°, to give 17.2 g (81%) of *N*-(4-tolylsulfonylmethyl)formamide, mp 108–111°. A solution of this product (16.00 g, 75 mmol) in 100 mL of dry THF was cooled to –20° under nitrogen. Diisopropylamine (34 mL, 242 mmol) was added all at once, followed by POCl₃ (8.6 mL, 90 mmol) over 20 minutes, keeping the temperature between –10 and –20°. After stirring for 1 hour at 0°, the mixture was poured into a cold solution of potassium carbonate (20.7 g, 150 mmol) in 500 mL of water. After 10 minutes the solid was collected, washed with water (6 × 50 mL) and dried in vacuum over CaCl₂ to give 13.44 g of a brown solid, mp 96–110°. The crude product was dissolved in CH₂Cl₂ (50 mL) and filtered through a short column of silica (15 g), using CH₂Cl₂ (100 mL). The combined filtrates were concentrated to dryness. Crystallization from methanol (60 mL) gave 10.0 g (68%) of TosMIC, mp 116–117° (dec.). Some characteristic data of TosMIC are: IR (Nujol) 2150 (N = C), 1320 and 1155 cm⁻¹ (SO₂); ¹H NMR (CDCl₃) δ 2.43 (s, CH₃), 4.53 (s, CH₂); ¹³C NMR (CDCl₃) 61.1 (CH₂), 165.7 (N = C); estimated p*K*_a 13–15; CAS Registry Number 36635–61–7.



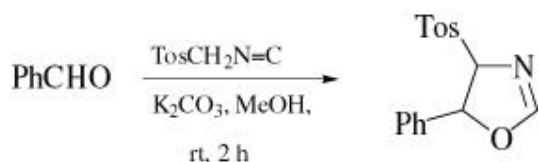
12.1.2. 2-Cyanoadamantane (Reductive Cyanation of a Ketone) (28, 32)

Solid potassium *tert*-butoxide (28.0 g, 0.24 mol, 95%) was added portionwise to a stirred and cooled solution of adamantanone (15.0 g, 0.10 mol) and TosMIC (25.0 g, 0.13 mol) in a mixture of 350 mL of 1,2-dimethoxyethane (DME) and 10 mL (0.17 mol) of absolute ethanol while keeping the temperature between 5 and 10°. Stirring was continued, first for 30 minutes without cooling, then for 30 minutes at 35–40°. The suspension thus obtained was cooled to room temperature with stirring. The precipitate (potassium *p*-toluenesulfinate) was removed and washed with DME. The combined DME solutions were concentrated to 25–35 mL and purified by flushing the concentrate over a 5-cm thick layer of alumina (ca. 200 g, on a Büchner funnel) with 250 mL of petroleum ether (bp 40–60°). Removal of the solvent provided 14–15 g (87–93%) of near-white 2-cyanoadamantane, mp 160–180° (sealed tube). Despite the wide melting range, this material is over 99.8% pure according to GLC (2-m ES-30 column, 190°). Charcoal treatment gave completely white material, melting in the same range.



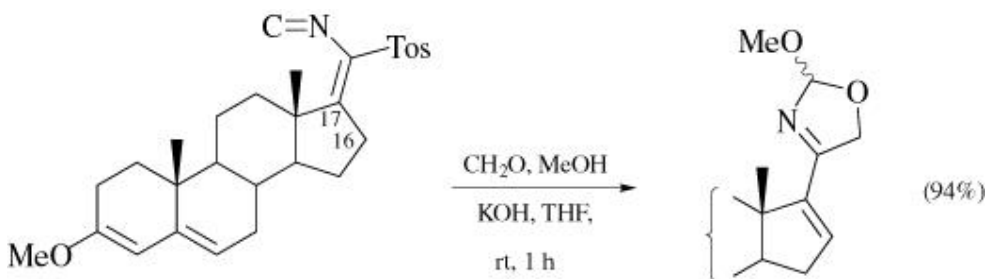
12.1.3. 2-*tert*-Butyl-5-cyanomethylthiophene (Reductive Cyanation of an Aldehyde) (64)

A solution of TosMIC (1.95 g, 10.0 mmol) in dry THF (10 mL) was added dropwise to a mixture of potassium *tert*-butoxide (1.12 g, 0.01 mol) in dry THF (10 mL) at –20° under argon. After the mixture was stirred for 30 minutes, 2-*tert*-butyl-5-thiophenecarboxaldehyde (1.68 g, 10.0 mmol) in dry THF (20 mL) was added dropwise. After the mixture was stirred for 30 minutes at –20°, 20 mL of methanol was added. Next, the mixture was refluxed for 15 minutes at 80° and then concentrated to dryness. The residue was treated with water (18 mL) and acetic acid (0.76 mL) and extracted with dichloromethane (3 × 10 mL). The product was obtained as an oil upon chromatography on silica with cyclohexane/ethyl acetate, 8:2. Yield 89%; IR (KBr) 2250 cm⁻¹ (CN); ¹H NMR (80 MHz, CDCl₃) δ 6.50 (d, *J* = 3.7 Hz, 1 H), 6.15 (d, *J* = 3.7 Hz, 1 H), 3.75 (s, 2 H), 1.30 (s, 9 H). Anal. Calcd. for C₁₀H₁₃NS : C, 66.99; H, 7.30; N, 7.80. Found: C, 66.58; H, 7.30; N, 7.77.



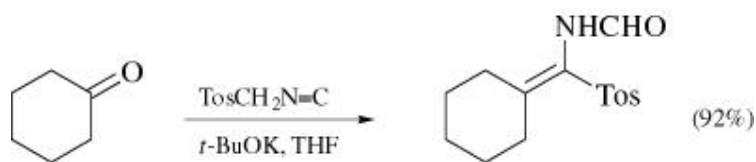
12.2. 5-Phenyl-4-tosyl-2-oxazoline (Reaction of an Aldehyde with TosMIC) (31)

Potassium carbonate (14 mg, 2 mol %) was added to a stirred mixture of TosMIC (0.98 g, 5.0 mmol), benzaldehyde (0.53 g, 5.0 mmol), and methanol (12.5 mL) at room temperature. After 2 hours, water (5 mL) was added and the mixture was stirred for another hour at 0°. The solid was collected, washed with water, and dried in vacuum to give 1.36 g (90%) of product, mp 110–111°; IR (Nujol) 1611 (C = N), 1310, 1153 and 1114 cm⁻¹ (SO₂); ¹H NMR (200 MHz, CDCl₃) δ 2.47 (s, 3 H), 5.05 (d, *J* = 6 Hz, 1 H), 6.07 (d, *J* = 6 Hz, 1 H), 7.23 (s, 1 H), 7.35–7.43 (m, 7 H), 7.84 and 7.88 (lower half of AB-q, 2 H); HRMS, *m/z* 301.077 (M⁺) (calculated 301.077).



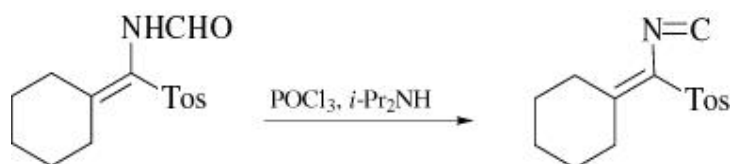
12.2.1. (2*ϕ*R)- and (2*ϕ*S)-3-Methoxy-17-(2-methoxy-3-oxazolin-4-yl)-androsta-3,5,16-triene (33) (Reaction of a Monosubstituted TosMIC Derivative with an Aldehyde and Methanol) (70)

Powdered potassium hydroxide (1.3 g, 22 mmol) was added to a stirred, ice cooled mixture of (*E*)-17-(isocyanatosylmethylene)-3-methoxyandrosta-3,5-diene (54) (32, 2.38 g, 5.0 mmol), 37% aqueous formaldehyde (0.7 mL, 9.0 mmol), methanol (1 mL, 25 mmol), and THF (35 mL). The ice bath was removed, stirring was continued for 1 hour at room temperature, and Na₂SO₄ (5 g) was added to the reaction mixture. After 5 minutes the mixture was filtered through a layer of alumina (neutral, act. II/III; 2 × 8 cm i.d.) with CH₂Cl₂ to give 1.80 g (94%) of crude title product, mp 118–122°. Analytically pure product was obtained by crystallization from CH₂Cl₂/Et₂O, mp 123–128°; IR (KBr) 1655, 1630 cm⁻¹ (C = N); ¹H NMR δ 0.8–2.6 (m), 1.04 (s), 1.02 (s), 3.35 and 3.36 (2 × s, ratio 2:1, CH₃OC₂), 3.57 (s), 4.6–4.8 (m), 5.14 (s), 5.24 (m), 6.28 (m), 6.55 (m); ¹³C NMR δ 168.9, 168.7, 155.4, 147.2, 141.4, 141.2, 122.4, 122.2, 117.6, 98.5, 73.4, 56.9, 54.3, 51.9, 48.7, 46.9, 35.4, 34.8, 33.6, 32.5, 31.5, 30.2, 25.2, 20.8, 18.8, 15.9. Anal. Calcd. for C₂₄H₃₃NO₃ (383.536): C, 75.16; H, 8.67; N, 3.65. Found: C, 75.1; H, 8.7; N, 3.9.



12.2.2. *N*-(Cyclohexylidenetosylmethyl)formamide (Reaction of TosMIC with a Ketone in a Nonprotic Solvent) (36, 63)

A solution of TosMIC (9.80 g, 50 mmol) in THF (50 mL) was added dropwise to a stirred solution of potassium *tert*-butoxide (6.26 g, 55 mmol) in THF (50 mL) at -35° . After 5 minutes, the reaction mixture was cooled to -70° and a solution of cyclohexanone (4.90 g, 50 mmol) in THF (50 mL) was added dropwise, then the temperature was allowed to rise to -40° . After 30 minutes, the reaction mixture was poured into ice-water (150 mL) and the mixture was neutralized with acetic acid, then extracted with Et₂O (100 mL). The organic layer was washed with sodium carbonate solution (20%, 50 mL), brine (30 mL), dried (Na₂SO₄), and concentrated. Crystallization from methanol gave 13.48 g (92%) of *N*-(cyclohexylidenetosylmethyl)formamide. Analytically pure material was obtained by crystallization from EtOH, mp 132° ; IR (KBr) 3310 (NH), 1690 (C = O), 1630 (C = C), 1280 and 1135 cm⁻¹ (SO₂); ¹H NMR (CDCl₃) δ 8.11 (s, CHO). Anal. Calcd. for C₁₅H₁₉NO₃S (293.4): C, 61.41; H, 6.53. Found: C, 61.36; H, 6.50.

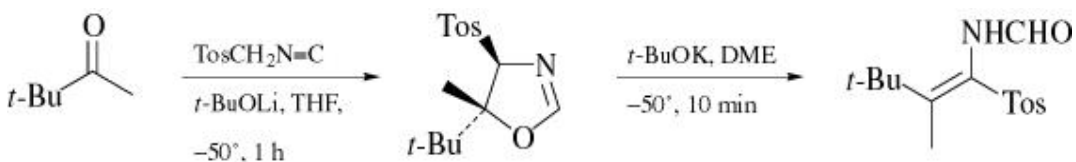


12.2.3. (Isocyanotosylmethylidene)cyclohexane (Dehydration of an Unsaturated Formamide) (63, 86)

A solution of POCl₃ (2.05 mL, 22 mmol) in THF (20 mL) was added dropwise to a stirred solution of *N*-(cyclohexylidenetosylmethyl)formamide (5.90 g, 20 mmol) and diisopropylamine (8.0 mL, 57 mmol) in THF (60 mL). The temperature was maintained between -35 and -30° . After the addition, the temperature was allowed to rise to -20° . After 30 minutes, a solution of sodium carbonate (20%, 20 mL) was added at such a rate that the temperature was kept below 5° . After 1 hour, diethyl ether (70 mL) and water (70 mL) were added. The organic layer was washed with water (2 \times 25 mL), with aqueous sodium carbonate solution (20%, 15 mL), and brine (20 mL), and dried

(Na₂SO₄). Removal of solvent (below 25°) gave 4.95 g (90%) of product which was analytically pure after one crystallization from methanol, mp 115° (dec.); IR (Nujol) 2180 (N = C), 1610 (C = C), 1360 and 1170 cm⁻¹ (SO₂). Anal. Calcd. for C₁₅H₁₇NO₂S: C, 65.43; H, 6.22; N, 5.09, S, 11.64. Found: C, 65.0; H, 6.2; N, 5.0; S, 11.6.

In general, it may be advantageous to filter the Et₂O solution over a short (4-cm) column of alumina, to replace the process of drying over Na₂SO₄. One author (63) assumed that traces of POCl₃ in Et₂O solution may cause decomposition of the isocyanide, especially when the temperature increased during removal of the solvent.



12.2.4. *trans*-5-*tert*-Butyl-5-methyl-4-tosyl-2-oxazoline and (*E*)-*N*-(2,3,3-Trimethyl-1-tosyl-1-butenyl)formamide (Reaction of TosMIC with a Sterically Screened Ketone by the Two-step/Two-base Approach) (55)

n-Butyllithium (7 mL, 1.6 M solution in hexane, ca. 10 mmol) was added to a stirred solution of TosMIC (1.95 g, 10.0 mmol) in THF (25 mL) at -80°. *tert*-Butyl alcohol (1.0 mL, 11 mmol) was added to the mixture, followed after 5 minutes by 3,3-dimethyl-2-butanone (1.0 g, 10 mmol). The temperature was raised to -50° and the mixture was stirred for 1 hour at that temperature. The mixture was then poured into water (200 mL) and the solution was extracted with dichloromethane (3 × 50 mL). The combined extracts were dried (MgSO₄) and concentrated to give 2.91 g (99%) of the oxazoline, mp 123–127°. Analytically pure material was obtained after one crystallization from Et₂O, mp 127°; IR (Nujol) 1623 (C = N), 1322, 1155 cm⁻¹ (SO₂); ¹H NMR (CDCl₃) δ 0.98 (s, 9 H), 1.85 (s, 3 H), 2.42 (s, 3 H), 4.77 (d, ^{1,4}J = 2 Hz, 1 H), 6.92 (d^{1,4}J = 2 Hz, 1 H), 7.20, 7.33, 7.72 and 7.85 (AB q, 4 H). Anal. Calcd. for C₁₅H₂₁NO₃S (295.399): C, 60.99; H, 7.17; N, 4.74; S, 10.85. Found: C, 61.10; H, 7.15; N, 7.74; S, 10.91.

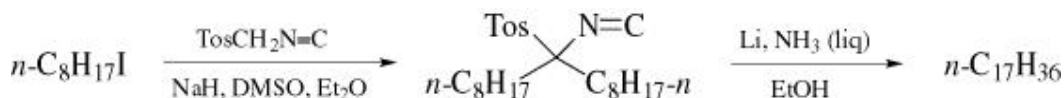
Potassium *tert*-butoxide (0.15 g, 1.3 mmol) was added to a stirred solution of the oxazoline (0.295 g, 1.00 mmol) in DME at -50°. After stirring for 10 minutes at -50°, the mixture was poured into water (50 mL) and was then extracted with EtOAc (3 × 15 mL). The combined extracts were washed with water, dried over Na₂SO₄, and concentrated to give 0.21 g (71%) of (*E*)-*N*-(2,3,3-trimethyl-1-tosyl-1-butenyl)formamide as an oil. Analytically pure

material (0.18 g) was obtained by crystallization from Et₂O/petroleum ether, mp 112–113°; IR (neat) 3400 (NH), 1700 (C = O), 1310, 1150 cm⁻¹ (SO₂); ¹H NMR CDCl₃ δ 1.20 (s, 9 H), 2.0 (br s, 1.5 H), 2.25 (br s, 1.5 H), 2.40 (s, 3 H), 6.7–8.2 (m, 6 H). Anal. Calcd. for C₁₅H₂₁NO₃S (295.399): C, 60.99; H, 7.17; N, 4.74; S, 10.85. Found: C, 60.93; H, 7.19; N, 7.73; S, 10.79.



12.2.5. 1-Tosylcyclobutyl Isocyanide (Intramolecular Dialkylation of TosMIC) (148)

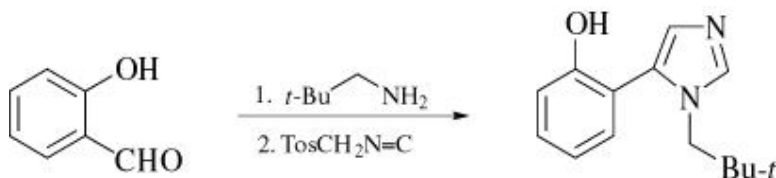
Sodium hydride (55–60% in mineral oil; 24 g, ~0.58 mol) was freed from mineral oil using dry petroleum ether (bp 40–60°) under nitrogen in a 2-L, three-necked flask, then dry DMSO (500 mL) and Et₂O (175 mL) were added. A solution of TosMIC (39.2 g, 0.20 mol) and 1,3-dibromopropane (48.5 g, 0.24 mol) in a mixture of dry DMSO (125 mL) and Et₂O (65 mL) was added over 45–60 minutes to the mechanically stirred suspension. During the addition the reaction mixture started to reflux and sodium bromide began to separate near the end. Stirring was continued for 1 hour, then water (150 mL) was added slowly. The mixture was extracted with Et₂O (2 × 250 mL, 1 × 150 mL and 1 × 100 mL), the combined extracts were washed with brine (3 × 100 mL), and dried over anhydrous Na₂SO₄. The Et₂O solution was concentrated to give a solid residue which was stirred with 100 mL of Et₂O for 10 minutes. After addition of petroleum ether (bp 40–60°, 100 mL) and overnight cooling at –20°, the product was collected; yield 33.3 g (71%), mp 95–97° (dec.). Analytically pure material was obtained from ethanol, mp 97°; IR (Nujol) 2190 (N = C), 1340, 1170 and 1150 cm⁻¹ (SO₂); ¹H NMR CDCl₃ δ 2.48 (s, 3 H), 1.8–3.6 (m, 6 H), 7.38, 7.85 (2 d, J = 8 Hz, 4 H); ¹³C NMR CDCl₃ δ 166.4 (s, N = C), 145.9 (s), 129.8 (d), 129.5 (d), and 129.2 (s, C-arom), 73.5 (s, 1-C), 31.0 (t, 2-C), 21.1 (q, ArCH₃), 13.9 (t, 3-C). Anal. Calcd. for C₁₂H₁₃NO₂S (235.3): C, 61.25; H, 5.57; N, 5.97; S, 13.62. Found: C, 61.27; H, 5.64; N, 6.05; S, 13.63.



12.2.6. 9-Isocyano-9-tosylheptadecane and *n*-Heptadecane (Dialkylation of TosMIC and Reduction of the Product; TosMIC as CH₂ Connector) (105)

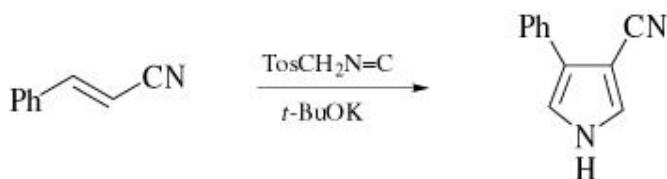
To a suspension of prewashed sodium hydride (0.528 g, 22 mmol) in a mixture of DMSO (3 mL) and Et₂O (15 mL) was added TosMIC (1.95 g, 10 mmol) in Et₂O (15 mL) at room temperature. After 10 minutes, *n*-octyl iodide (4.8 g, 20 mmol) in Et₂O (15 mL) was added dropwise, the mixture was stirred for 3 hours, and poured into water. The organic layer was separated and the aqueous layer was extracted with Et₂O. The combined extracts were washed with water and brine, and dried (Na₂SO₄). After removal of the solvent, 3.77 g (90%) of 9-isocyano-9-tosyl-heptadecane was obtained as a gummy substance; IR (neat) 2130 cm⁻¹ (N = C); ¹H NMR CCl₄) δ 0.90 (distorted t, 6 H), 1.3 (m, 28 H), 2.45 (s, 3 H), 7.23 (d, *J* = 8 Hz, 2 H), 7.68 (d, *J* = 8 Hz, 2 H).

To freshly distilled liquid ammonia (50 mL) at -33° was added lithium (0.050 g, 7.0 mmol) in one portion, followed by 9-isocyano-9-tosylheptadecane (0.294 g, 0.70 mmol) in a mixture of Et₂O (3 mL) and ethanol (0.12 mL). After 2 hours, the ammonia was allowed to evaporate. Then, water was added and the mixture was extracted with diethyl ether (5 × 10 mL). The combined extracts were washed with water (20 mL), with brine (20 mL), dried (Na₂SO₄), and concentrated. Distillation of the residue (pot temperature 125–135°, 1 mm Hg) afforded 0.156 g (93%) of heptadecane as a colorless liquid; ¹H NMR (CCl₄) δ 0.90 (distorted t, 6 H), 1.27 (m, 30 H).



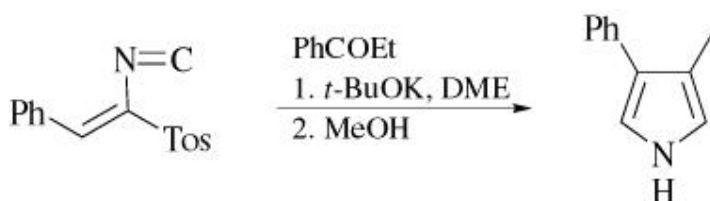
12.2.7. 5-(2-Hydroxyphenyl)-1-neopentylimidazole (Reaction of TosMIC with an Aldimine) (121)

A mixture of salicylaldehyde (0.65 g, 5.3 mmol), neopentylamine (1.0 g, 11.5 mmol), and anhydrous magnesium sulfate (3.6 g, 30 mmol) was heated at reflux for 2 hours. The magnesium sulfate was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was dissolved in 20 mL of methanol, and to the mixture was added potassium carbonate (3.5 g, 25 mmol) and TosMIC (1.2 g, 6.2 mmol). After heating at reflux for 2 hours, the solvent was evaporated and water (50 mL) was added to the residue. The precipitate was collected by filtration and recrystallized from ethanol and water to afford 1.0 g (82%) of the title product, mp 247–248°; ¹H NMR CDCl₃) δ 0.72 (s, 9 H), 3.76 (s, 2 H), 6.7–7.6 (m, 7 H).



12.2.8. 3-Cyano-4-phenylpyrrole (Reaction of a Michael Acceptor with TosMIC) (136)

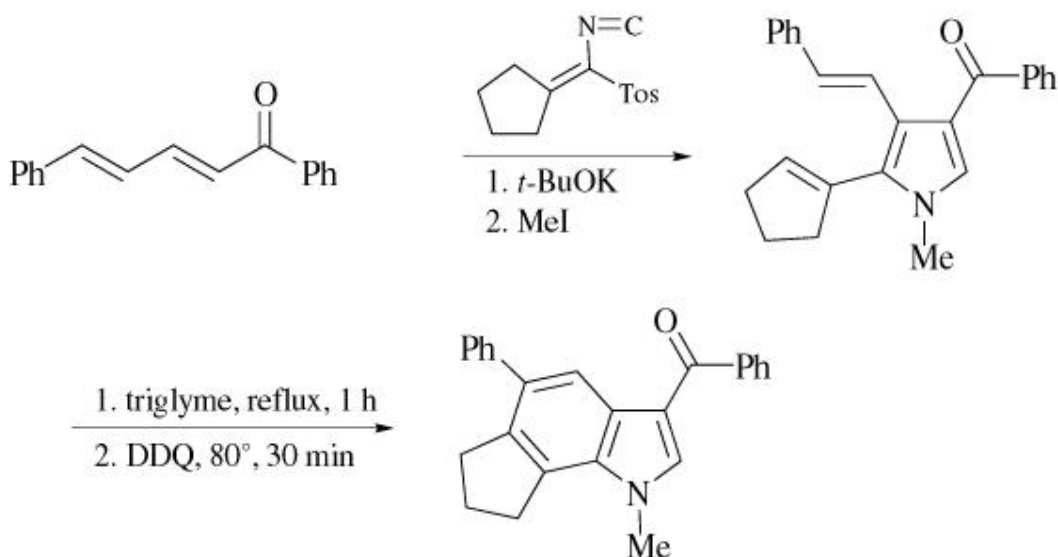
To a stirred suspension of potassium *tert*-butoxide (1.05 g, ~13 mmol) in THF (10 mL) at -30° was added in 2 minutes a solution of TosMIC (1.17 g, 6.0 mmol) in THF (10 mL). The temperature rose to -25° . The mixture was stirred for 4 minutes at -30° before a solution of cinnamionitrile (0.77 g, 6.0 mmol) in THF (10 mL) was added over 4 minutes. Stirring was continued for 15 minutes at -10° , and then the mixture was poured on 50 g of ice. Most of the THF was removed while the temperature was kept below 35° . The off-white precipitate was collected, washed with water, and dried in vacuum to give 0.89 g (88%) of product, mp $124\text{--}125^{\circ}$; IR (Nujol) 3360 (NH), 2290 cm^{-1} (CN); $^1\text{H NMR}$ CDCl_3 δ 6.87 (apparent t, $J = 2$ Hz, 1 H), 7.1–7.8 (m, ca. 6 H), 9.0 (br s, 1 H).



12.2.9. 3-Methyl-4-phenylpyrrole (Reaction of a Michael Donor with a 1-Iso-cyano-1-tosyl-1-alkene) (136)

A solution of (*E*)-1-isocyano-2-phenyl-1-tosylethene (86) (0.566 g, 2.0 mmol) and propiophenone (0.536 g, 4.0 mmol) in DME (10 mL) was added over 10 minutes to a mixture of potassium *tert*-butoxide (0.70 g, 6.2 mmol) and DME (5 mL) at 0° and stirred for 1 hour at 20° . Methanol (0.5 mL) was added, and the mixture was stirred for another 5 minutes and then poured into ice-water (80 mL). This mixture was extracted with CH_2Cl_2 (30, 20 and 10 mL). The combined extracts were washed with brine, dried (MgSO_4), and concentrated. Column chromatography on alumina [activity grade II-III, Et_2O /petroleum ether (bp $40\text{--}60^{\circ}$) 1:5] gave 0.23 g (73%) of the title compound as a colorless oil; IR (neat) 3500 cm^{-1} (NH); $^1\text{H NMR}$ CDCl_3 δ 2.13 (s, 3 H), 6.19–6.38 (m, 1 H),

6.49 (apparent t, $J = 2$ Hz, 1 H), 6.7–8.0 (m, ca. 6 H); HRMS, m/z 157.092 (M⁺) (calculated 157.089).



12.2.10. (E)-4-Benzoyl-2-(cyclopent-1-enyl)-1-methyl-3-(2-phenylethenyl)pyrrole and

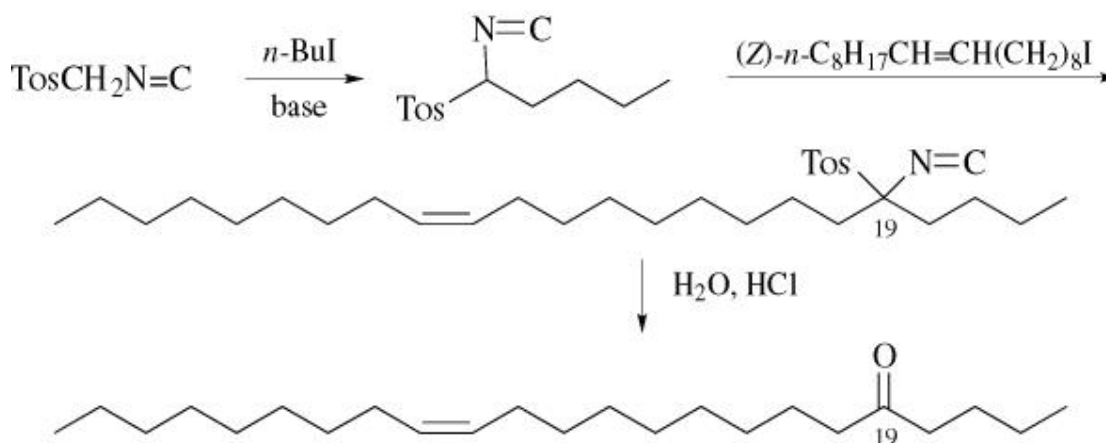
3-Benzoyl-7,8-dihydro-1-methyl-5-phenyl-6H-cyclopent[g]indole

(Formation of a 2,3-Dialkenylpyrrole from a TosMIC Derivative and a Michael Acceptor, Followed by Ring Closure and Dehydrogenation to an Indole) (128)

To a suspension of potassium *tert*-butoxide (1.12 g, 10 mmol) in THF (15 mL), precooled to -60° , was added dropwise a solution of (isocyanatosylmethylidene)cyclopentane (181a) (2.61 g, 10 mmol) in 20 mL of THF while maintaining the temperature below -50° . The reaction mixture turned into a transparent orange solution, which was stirred for an additional 10 minutes at -50° . A solution of 1,5-diphenylpenta-2,4-dien-1-one (2.34 g, 10 mmol) in 20 mL of THF was added. The temperature was increased to -20° . Stirring was continued for 1 hour without further cooling. Then the reaction mixture was concentrated in vacuum (at 20°), and the solid residue was suspended in 30 mL of benzene. Methyl iodide (2.82 g, 20 mmol) was added, and the mixture was treated with 30 mL of 50% aqueous KOH containing 0.25 g (1.1 mmol) of benzyltriethylammonium chloride. The reaction mixture was vigorously stirred for 1 hour at room temperature. The benzene layer was separated, washed with 10% aqueous NH_4Cl (50 mL) and then twice with water (50 mL each), and dried (MgSO_4), to give after concentration and crystallization from ethanol, 2.96 g (84%) of (E)-4-benzoyl-2-(cyclopent-1-enyl)-1-methyl-3-(2-phenylethenyl)pyrrole as

pale yellow crystals, mp 141–142°; IR (KBr) 2905, 2838, 1620 (C = O, C = C), 1500, 1420, 1345, 1221 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.8–2.3 (m, 2 H), 2.4–2.8 (m, 4 H), 3.48 (s, 3 H), 5.9–6.0 (m, 1 H), 6.89 (s, 1 H), 7.0–7.4 (m, 10 H), 7.7–7.9 (m, 2 H). Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{NO}$ (353.18): C, 84.99; H, 6.52; N, 3.97. Found: C, 85.00; H, 6.57; N, 4.00.

A solution of the foregoing product (1.76 g, 5.0 mmol) in 20 mL of dry triglyme was gently refluxed for 1 hour. The yellow-orange solution was cooled to approximately 80°, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.18 g, 5.2 mmol) was added. The dark red mixture was stirred at 80° for 30 minutes and then poured into 200 mL of cold water. The mixture was stirred for 30 minutes. The precipitate (2 g) was collected, washed several times with cold water, and dried in air. Purification was performed over alumina (Brockmann 90, II/III, 200 g; 8:1 $\text{CH}_2\text{Cl}_2/n$ -pentane) to give 1.46 g (83%) of colorless prisms, which were recrystallized from ethanol: mp 172–173°; IR (KBr) 3050, 2940, 2840, 1610 (C = O), 1520, 1450, 1440, 1362, 1225, 1140, 960 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 2.01 (quintet, $J = 4.2$ Hz, 2 H), 2.89 (t, $J = 4.2$ Hz, 2 H), 3.21 (t, $J = 4.2$ Hz, 2 H), 3.76 (s, 3 H), 7.0–7.3 (m, 9 H), 7.4–7.6 (m, 2 H), 8.16 (s, 1 H); Anal. Calcd. for $\text{C}_{25}\text{H}_{21}\text{NO}$ (351.16): C, 85.43; H, 6.03; N, 3.99. Found: C, 84.86; H, 5.91; N, 3.99.

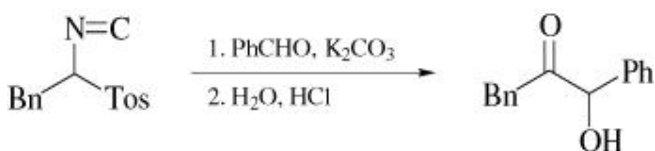


12.2.11. (Z)-19-Isocyano-19-tosyltricos-9-ene and (Z)-Tricos-9-en-19-one (Alkylation of a Monosubstituted TosMIC Derivative and Hydrolysis of a Disubstituted TosMIC Derivative. TosMIC as CO Connector) (107)

Potassium *tert*-butoxide (2.7 g, 24 mmol) was added over 5 minutes to a solution of 1-tosyl-*n*-pentyl isocyanide (90) (5.02 g, 20 mmol) and (Z)-octadec-9-enyl iodide [7.90 g, ca. 20 mmol, prepared from oleyl alcohol (Merck-Schuchhardt, technical grade 88%)] in a mixture of DMSO (20 mL) and

Et₂O (50 mL) at 10° under nitrogen. After stirring for 20 minutes at 10°, the reaction mixture was poured into a 1% solution of NH₄Cl in water (500 mL). The mixture was extracted three times with Et₂O (100, 75, and 25 mL). The combined extracts were washed with brine, dried (Na₂SO₄), and concentrated to give 10.0 g of (Z)-19-isocyano-19-tosyltricos-9-ene as a gummy material.

A solution of crude (Z)-19-isocyano-19-tosyltricos-9-ene (5.0 g, ca. 10 mmol) in Et₂O (50 mL) was stirred with concentrated HCl (5 mL) at 10° for 15 minutes. The organic layer was washed with a 20% aqueous solution of sodium carbonate (25 mL), and the aqueous phase was extracted with Et₂O (2 × 25 mL). The organic layer and extracts were combined, dried (Na₂SO₄), and concentrated to give 3.3 g of crude product, which was purified by column chromatography on silica (elution with CH₂Cl₂-pentane, 1:2). Yield 3.0 g (ca. 90%) as a viscous oil; IR (neat) 1715 cm⁻¹ (C = O); ¹H NMR (300 MHz, CDCl₃) δ 0.85 (distorted t, J = 4 Hz, 6 H), 1.25 (m, 24 H), 1.52 (m, 4 H), 1.97 (m, 4 H), 2.35 (t, 4 H), 5.3 (t J = 4 Hz, 2 H).



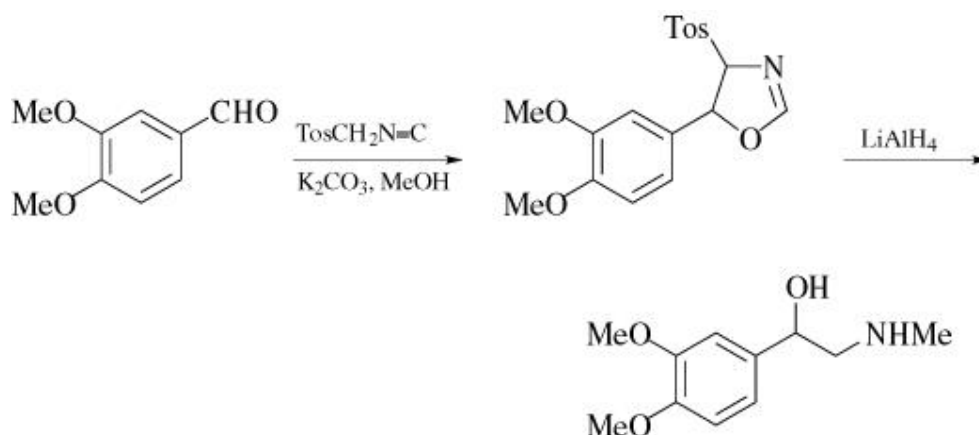
12.2.12. 1,3-Diphenyl-1-hydroxypropan-2-one (Synthesis of a Tosyloxazoline, Followed by Hydrolysis to a Hydroxyketone) (73)

Powdered potassium carbonate (0.10 g, 0.7 mmol) was added to a stirred solution of 2-phenyl-1-tosylethyl isocyanide (73) ("Benzyl-TosMIC", 2.85 g, 10.0 mmol) and benzaldehyde (1.06 g, 10.0 mmol) in 20 mL of methanol at 30°. After 5 minutes, the mixture was cooled to 0° at which temperature the tosyloxazoline started to precipitate. Addition of concentrated HCl (1 mL) gave a clear solution, which was stirred for 10 minutes. Water (5 mL) was added and the mixture was neutralized with a 30% aqueous NaOH solution. The mixture was cooled to -10° for 1 hour and the separated solid was collected, dried, and crystallized from Et₂O/pentane (5:1) to give 1.54 g (68%) of the title compound, mp 113–114.5°; ¹H NMR (CDCl₃) δ 3.64 (s, 2 H), 4.20 (br s, 1 H), 5.18 (s, 1 H), 7.0–7.4 (m, 10 H).

12.2.13. N-Methyl-2-(3,4-dimethoxyphenyl)-2-hydroxyethylamine (Reaction of TosMIC with an Aldehyde, Followed by Reduction with Lithium Aluminum Hydride) (73)

A solution of TosMIC (1.95 g, 10.0 mmol) and 3,4-dimethoxybenzaldehyde (1.66 g, 10.0 mmol) in 20 mL of methanol was stirred with 0.1 g powdered potassium carbonate (0.10 g, 0.7 mmol) for 10 minutes at room temperature

and for 30 minutes at 0°, then kept for 2 hours at -20°. The solid oxazoline was collected and dried (40°, 0.1 mm Hg, 30 minutes). To a solution of the crude



oxazoline in 50 mL of dry THF at 0° was added lithium aluminum hydride (0.80 g, 23.5 mmol) in small portions. The mixture was stirred for 30 minutes at 25°. After cooling to 0°, 1.5 mL of water was added. THF (50 mL) was added and the mixture was filtered. The aluminum salts were washed with 50 mL of THF and the combined filtrates were concentrated. Crystallization of the residue from hexane/acetone (2:1) gave 1.49 g (71%) of the title compound; mp 102–103.5°; ¹H NMR (CDCl₃) δ 2.40 and 2.46 (br s + s, 5 H, NH, OH and CH₃), 2.75 (m, 2 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 4.68 (m, 1 H), 6.9 (m, 3 H).

13. Tabular Survey

The material presented in the tables is based on a *Chemical Abstracts* search covering the period 1967 (the year that TosMIC was discovered) to January 1996, and on further information available to the authors. Reference is made to all pertinent full papers that have been uncovered. Preliminary papers, as a rule, are listed only when they provide data not given in the corresponding full papers. The rather extensive patent literature is treated selectively. Only patents that provide material other than “more of the same” are cited.

The *Chemical Abstracts* search has been performed with the use of both the CAS Registry Numbers of TosMIC and its isotopically labeled counterparts, as well as the essential structure element: $\text{SO}_2 - \text{C} - \text{N} = \text{C}$. The outcome of the computer search sometimes was misleading, and needed a critical evaluation. Not only have isocyanides occasionally been erroneously named isocyanates by authors, reviewers, or abstractors, they have also been formulated mistakenly as $-\text{C} \equiv \text{N}$ or $-\text{N} = \text{C} = \text{O}$. Further, the sulfonyl group (SO_2) has sometimes been confused with the sulfonate group (SO_3).

The integral results of the “Synthetic Uses of TosMIC” are collected in eighteen tables, which follow the sequence of the various sections. The discussion of the synthesis of indoles is not accompanied by a table on indoles, since indoles are secondary products of the use of TosMIC. When closely related products are derived from different groups of substrate molecules, a subdivision of Tables is employed, as for example in Tables [I-A](#), [I-B](#), and [I-C](#). The sequence within the tables is based on increasing carbon count of the substrate molecules.

Standard abbreviations used in the Tables are the following:

AIBN	azobis(isobutyronitrile)
—	data not provided
aq	aqueous
BTEAC	benzyltriethylammonium chloride
Dabco	1,4-diazabicyclo[2.2.2]octane
de	diastereomeric excess
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide

DPA	diisopropylamine
ee	enantiomeric excess
Ether	diethyl ether
HMPA	hexamethylphosphoric triamide
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
NMM	<i>N</i> -methylmorpholine
sl add.	slow addition
TBAB	tetrabutylammonium bromide
TBAI	tetrabutylammonium iodide
TEA	triethylamine
THAI	tetrahexylammonium iodide
THF	tetrahydrofuran
THP	tetrahydropyranyl
Tos	4-tolylsulfonyl
Triton B	benzyltrimethylammonium hydroxide, 40% solution in methanol

Table IA. Cyanides from Ketones by Reductive Cyanation

[View PDF](#)

Table IB. Cyanides from Aldehydes by Reductive Cyanation

[View PDF](#)

Table IC. Carboxylic Acids and Esters from Ketones or Aldehydes via Reductive Cyanation

[View PDF](#)

Table II. Oxazolines from Ketones or Aldehydes

[View PDF](#)

Table IIIA. Oxazoles from Aldehydes

[View PDF](#)

Table IIIB. Tosyloxazoles from Carboxylic Acid Derivatives

[View PDF](#)

Table IV. 1-Formamido-1-tosylalkenes from Aldehydes or Ketones

[View PDF](#)

**Table VA. 1-Isocyano-1-tosylalkenes by Dehydration of
1-Formamido-1-tosylalkenes**

[View PDF](#)

**Table VB. 1-Isocyano-1-tosylalkenes by in situ Dehydration of
1-Formamido-1-tosylalkenes**

[View PDF](#)

**Table VC. 1-Isocyano-1-tosylalkenes from Aldehydes or Ketones by
Peterson Olefination**

[View PDF](#)

Table VI. Monoalkylation of TosMIC

[View PDF](#)

Table VIIA. Disubstituted Derivatives of TosMIC

[View PDF](#)

**Table VIIB. Disubstituted Derivatives of TosMIC from
1-Isocyano-1-Sulfonylalkenes**

[View PDF](#)

**Table VIIC. α -Isocyano- α -Tosyl Ketones from TosMIC Homologs and
Carboxylic Chlorides**

[View PDF](#)

Table VIIIA. Imidazoles from Aldimines

[View PDF](#)

Table VIIIB. 4-Tosylimidazoles from Imidoyl Chlorides or Isothiocyanates

[View PDF](#)

Table VIIIC. Imidazoles from 1-Isocyano-1-tosylalkenes

[View PDF](#)

Table IX. 1,2,4-Triazoles from Diazonium Salts

[View PDF](#)

Table X. Thiazoles from Thiocarbonyl Compounds

[View PDF](#)

**Table XI-A1. Pyrroles from TosMIC or TosMIC Homologs TosCHRN = C
and Michael Acceptors**

[View PDF](#)

**Table XI-A2. Pyrroles from TosMIC Homologs TosC(= CR₂)N = C and
Michael Acceptors**

[View PDF](#)

Table XIB. Pyrroles from 1-Isocyano-1-tosylalkenes and Michael Donors

[View PDF](#)

**Table XII. Ketones by Acid Hydrolysis of Disubstituted TosMIC
Derivatives**

[View PDF](#)

Table XIII. 1,2-Diketones from Acid Chlorides

[View PDF](#)

**Table XIV. α -Hydroxy Ketones and α -Hydroxy Aldehydes by Hydrolysis
of Oxazolines**

[View PDF](#)

Table XV. Alkanes, *N*-Methylamines, and Isocyanides by Reduction of TosMIC Derivatives

[View PDF](#)

Table XVI. β -Hydroxy-*N*-Methylamines by Reduction of 4-Tosyloxazolines

[View PDF](#)

Table XVII. α -Additions to the Isocyano Carbon of TosMIC

[View PDF](#)

Table XVIII. Cycloadditions to the Isocyano Carbon of TosMIC

[View PDF](#)

TABLE IA. CYANIDES FROM KETONES BY REDUCTIVE CYANATION



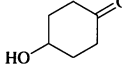
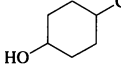




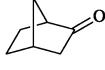
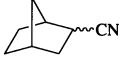


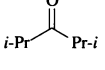

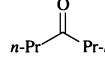

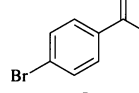
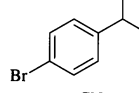
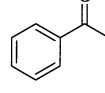



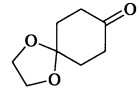
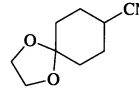
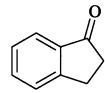

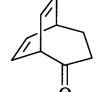

Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.
	(1.0)	<i>t</i> -BuOK (2), DME, rt, 1.5 h	 (80)	32,53
	(1.5)	<i>t</i> -BuOK (6), DME, <i>t</i> -BuOH, rt, 1 h	 (75)	182a
	(1.3)	<i>t</i> -BuOK (3.5), DMSO, rt, 17 h	 (70)	32
	(1.0)	<i>t</i> -BuOK (2), DME, rt, 1.5 h	" (36)	32,53
	(1.0)	1. <i>t</i> -BuOLi, THF, -50°, 1 h 2. <i>t</i> -BuOLi, THF, rt 10 min	" (85)	55
C₇ 	(1.05)	<i>t</i> -BuOK (2), THF, <i>t</i> -BuOH, 0°, 45 min	 (10)	182
	(1.3)	<i>t</i> -BuOK (3.5), DMSO, rt, 17 h	 (73) <i>endo:exo</i> = 4:3	32
	(1.3)	EtONa (1.3), DME, rt, 2.5 h	" (62) <i>endo:exo</i> = 1:1	32
	(1.1)	<i>t</i> -BuOK (2), DME, rt, 1.5 h	 (80)	32,53
	(3)	<i>t</i> -BuOK (7), HMPA, 45°, 70 h	 (65)	32
	(1.0)	<i>t</i> -BuOK (2), DME, rt, 1.5 h	" (<5)	32
	(1.2)	<i>t</i> -BuOK (2.5), DME, rt, 1.5 h	 (74)	32, 53
C₈ 	(1.0)	<i>t</i> -BuOK (2), DME, rt, 1.5 h	 (79)	32, 53
	(1.0)	<i>t</i> -BuOK (2), DME, rt, 1.5 h	 (68)	32
	(2)	<i>t</i> -BuOK (2), <i>t</i> -BuOH, DME, 0°, 45 min; rt, 1 h	" (80)	53
	(1.5)	<i>t</i> -BuOK (4), DMSO, rt, 24 h	 (70)	183
	(—)	—	 (>60)	67
	(—)	<i>t</i> -BuOK, 0°, 1 h; rt, 2 h	" (75)	184
C₉ 	(1.5)	EtONa (1.5), DME, EtOH, 0°, 1 h; rt, 2.5 h	 (58)	66
	(1.5)	<i>t</i> -BuOK (7), <i>t</i> -BuOH, DME, rt, 1 h	 (>54)	185

TABLE IA. CYANIDES FROM KETONES BY REDUCTIVE CYANATION (Continued)

Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.
	(1.3)	<i>t</i> -BuOK (2.5), EtOH, DME, rt, 1 h; 40°, 1 h	(68)	186
	(1.3)	<i>t</i> -BuOK (2.7), DMSO, rt	(63)	187
	(—)	—	(—)	188
	(1)	<i>t</i> -BuOK (2), <i>t</i> -BuOH, DME, 0°, 45 min; rt, 1 h	(90)	57
	(1)	<i>t</i> -BuOK (2), <i>t</i> -BuOH, DME, 0°, 45 min; rt, 1 h	(76)	189
	(3)	<i>t</i> -BuOK (7), HMPA, 45°, 170 h	No reaction	32
	(3)	<i>t</i> -BuOK (5), HMPA, rt, 21 h	(47)	32
	(1.3)	<i>t</i> -BuOK (2.4), DME, 35°, 1.5 h	(93)	32, 190
	(1.3)	<i>t</i> -BuOK (3.5), DMSO, rt, 17 h	" (84)	32
	(1.3)	EtONa (1.3), EtOH, DME, rt, 0.5 h	" (80)	191
	(1)	<i>t</i> -BuOK (2), DME, MeOH, 0 to 5°, 1 h	I + II (67); I>II	192
	(1)	<i>t</i> -BuOK (2), DME, MeOH, 0 to 5°, 1 h; 40°, 1 h	II (—)	192
	(3)	<i>t</i> -BuOK (7), DMSO, 45°, 70 h	(80) <i>endo:exo</i> = 1:4 or 4:1	32
	(3)	<i>t</i> -BuOK (7), HMPA, 45°, 17 h	" (73)	32
	(1.1)	<i>t</i> -BuOK (2), DME, rt, 1.5 h,	" (<5)	32
	(1)	<i>t</i> -BuOK (2), DME, <i>t</i> -BuOH, 0°; rt, 3 h	(57) <i>cis:trans</i> = 9:11	193

TABLE IA. CYANIDES FROM KETONES BY REDUCTIVE CYANATION (Continued)

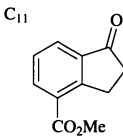
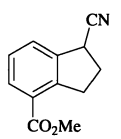
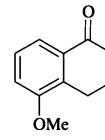
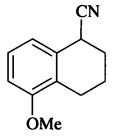
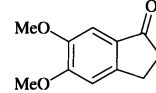
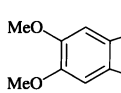
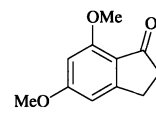
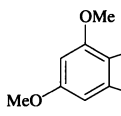
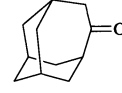
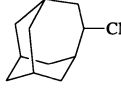
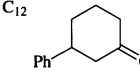
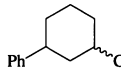
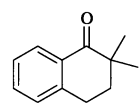
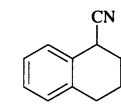
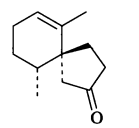
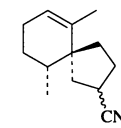
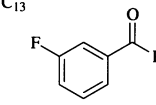
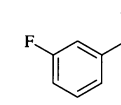
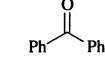
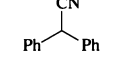
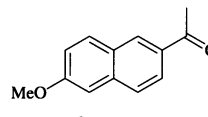
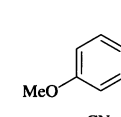
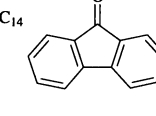
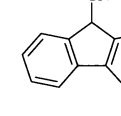
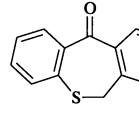
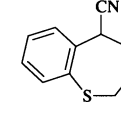
Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.
	(1.5)	EtONa (1.5), EtOH, DME, 0°, 1 h; rt, 5.5 h	 (37)	66
	(2)	<i>t</i> -BuOK (10), DME, <i>t</i> -BuOH, rt, 20 h	 (77)	194
	(1.3)	<i>t</i> -BuOK (7), THF, 0°, 1.5 h; rt, 72 h	 (63)	195
	(2)	<i>t</i> -BuOK (10), DME, <i>t</i> -BuOH, rt, 48 h	 (84)	195a
	(—)	—	 (37)	196
	(1)	<i>t</i> -BuOK (2), DME, 0°, 45 min; 20°, 1 h	 (74)	197
	(3)	<i>t</i> -BuOK (7), HMPA, 45°, 40 h	 (76)	32
	(—)	<i>t</i> -BuOK	 (80) ratio 3:2	198
	(1.4)	<i>t</i> -BuOK (5), DMSO, rt, 17 h	 (84)	199
	(1.3)	<i>t</i> -BuOK (3.5), DMSO, rt, 17 h	 (69)	32
	(1.5)	EtONa (1.5), EtOH, DME, 0°, 1 h; rt, 4 h	No reaction	66
	(1)	<i>t</i> -BuOK (2), <i>t</i> -BuOH, DME, -20°, 15 min; rt, 3.5 h	 (89)	200
	(2)	<i>t</i> -BuOK (6), THF, rt, 15 h	 (55)	201
	(1.3)	<i>t</i> -BuOK (3), DMSO, rt, 5.5 h	 (0) ^b	202

TABLE IA. CYANIDES FROM KETONES BY REDUCTIVE CYANATION (Continued)

Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.										
	(—)	<i>t</i> -BuOK (—), DME, 0°, 20 min; rt, 1 h	(52)	203										
	(1)	<i>t</i> -BuOK (1), THF, 0°, 1 h	(53)	205										
	(3)	<i>t</i> -BuOK (5), DME, <i>t</i> -BuOH, 0°, 0.5 h; rt, 8 h	(68) α:β = 22:78	206										
	(3)	<i>t</i> -BuOK (5), DME, <i>t</i> -BuOH, 0°, 0.5 h; rt, 12 h	(48) α:β = 1:1	206										
	(1.3)	<i>t</i> -BuOK (2.5), DME, EtOH, rt, 2 h	(22) + (33)	204										
	(1.5)	EtONa (1.5), EtOH, DME, 0°, 1 h; rt, 3 h	(50) X = H (50) X = 4-Br (37) X = 4-Cl (55) X = 4-F (28)	66										
	(1.5)	EtONa (1.5), EtOH, DME, 0°, 1 h; rt, 4 h	(46)	66										
	(1.3)	<i>t</i> -BuOK (2.5), DME, MeOH, 0°; 35-40°, 2 h	(39)	207										
	(3)	<i>t</i> -BuOK (7), DMSO, MeOH, rt, 1 h; 45°, 72 h	(72)	208										
	(1.1)	<i>t</i> -BuOK (2), THF, EtOH, -5°; rt, 1 h; 40°, 1 h	(73)	209										
	(2)	<i>t</i> -BuOK (10), DME, EtOH, rt, 3 h	I + II I + II (60) I:II = 4:6 I + II (27) I:II = 1:1 I + II (63) I:II = 3:7 II (36)	210										
			<table border="1"> <thead> <tr> <th>R</th> <th>R¹</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>Me</td> </tr> </tbody> </table>	R	R ¹	H	H	H	Me	Me	H	Me	Me	
R	R ¹													
H	H													
H	Me													
Me	H													
Me	Me													

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TABLE IA. CYANIDES FROM KETONES BY REDUCTIVE CYANATION (Continued)

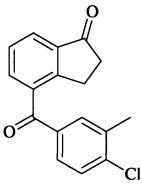
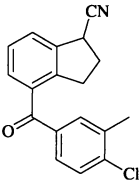
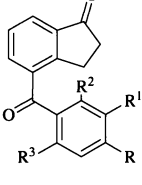
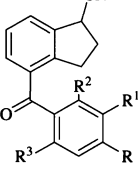
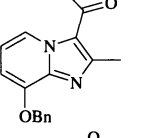
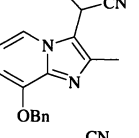
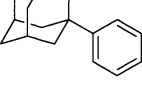
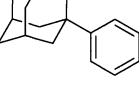
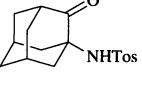
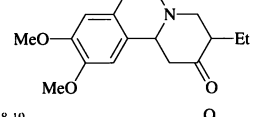
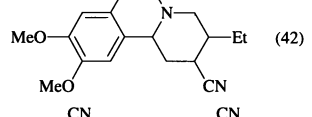
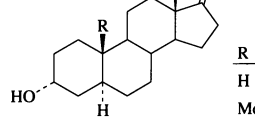
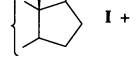
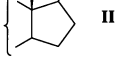
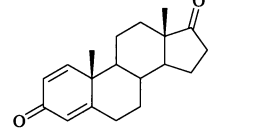
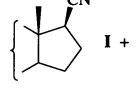
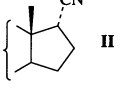
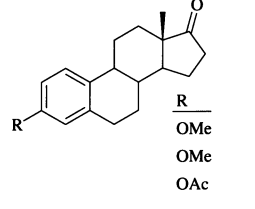
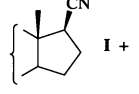
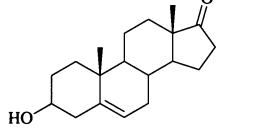
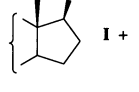
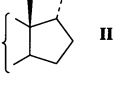
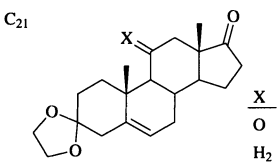
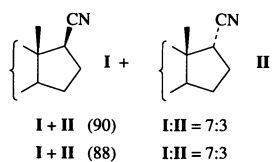
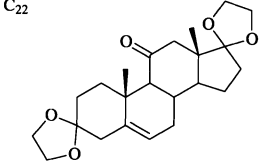
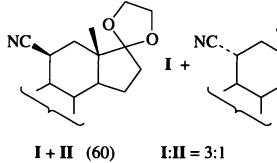
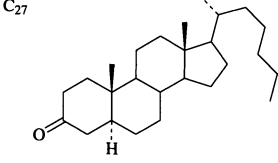
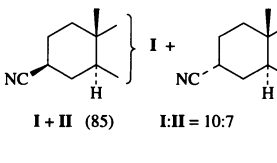
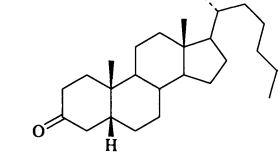
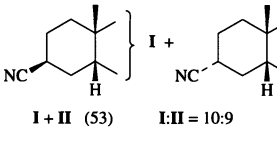
Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.																														
C ₁₇ 	(1.5)	EtONa (1.5), EtOH, DME, 0°, 1 h; rt, 3 h	 (53)	66																														
C ₁₇₋₂₀ 	(1.5)	EtONa (1.5), EtOH, DME, 0°, 1 h; rt, 3 h	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> <td>(45)</td> </tr> <tr> <td>Et</td> <td>H</td> <td>H</td> <td>H</td> <td>(41)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> <td>(29)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>Me</td> <td>(50)</td> </tr> <tr> <td>Bu-<i>t</i></td> <td>H</td> <td>H</td> <td>H</td> <td>(46)</td> </tr> </tbody> </table>	R	R ¹	R ²	R ³		Me	H	H	H	(45)	Et	H	H	H	(41)	Me	Me	H	H	(29)	Me	H	Me	Me	(50)	Bu- <i>t</i>	H	H	H	(46)	66
R	R ¹	R ²	R ³																															
Me	H	H	H	(45)																														
Et	H	H	H	(41)																														
Me	Me	H	H	(29)																														
Me	H	Me	Me	(50)																														
Bu- <i>t</i>	H	H	H	(46)																														
C ₁₇ 	(10)	<i>t</i> -BuOK (10), DME, <i>t</i> -BuOH, rt, 1 h	 (10)	211																														
	(3)	<i>t</i> -BuOK (7), DMSO, MeOH, rt, 1 h; 45°, 72 h	 (59)	208																														
	(1.3)	<i>t</i> -BuOK (2), DME, EtOH, rt, 14 h; 60°, 5 h	No reaction	212																														
	(1.2)	<i>t</i> -BuOK (10), DME, <i>n</i> -BuOH, rt, 1 h	 (42)	213																														
C ₁₈₋₁₉ 	(2)	<i>t</i> -BuOK (10), DME, <i>n</i> -BuOH, rt, 3 h	 I +  II I + II (52) I:II = 5:6 I + II (59) I:II = 2:3	210 210, 214																														
C ₁₉ 	(1.3)	EtONa (1.2), DME, rt, 2 h	 I +  II I + II (47) I:II = 1:1	32																														
C ₁₉₋₂₀ 	(1.3)	<i>t</i> -BuOK (3.5), DMSO, rt, 17 h	 I (69)	32																														
	(2)	<i>t</i> -BuOK (10), DME, <i>t</i> -BuOH, rt, 1 h	I + II (91), I:II = 3:2	56																														
	(—)	<i>t</i> -BuOK (xs), <i>t</i> -BuOH, DME	I + II (85), I:II = 2:1	215																														
	(2)	<i>t</i> -BuOK (10), DME, <i>t</i> -BuOH, rt, 1 h	 I +  II I + II (86) I:II = 7:3	56																														


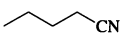
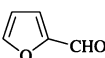
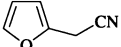
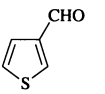
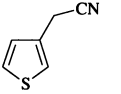
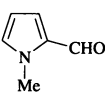
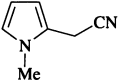
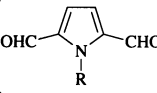
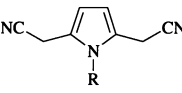
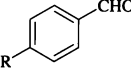
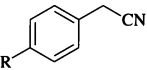
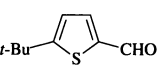
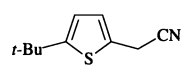
TABLE IA. CYANIDES FROM KETONES BY REDUCTIVE CYANATION (Continued)

Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.
 C ₂₁	(2)	<i>t</i> -BuOK (10), DME, <i>t</i> -BuOH, rt, 1 h	 I + II (90) I:II = 7:3 I + II (88) I:II = 7:3	56
 C ₂₂	(—)	<i>t</i> -BuOK (—), DME	 I + II (60) I:II = 3:1	216, 217
 C ₂₇	(1.3)	<i>t</i> -BuOK (2.5), DME, rt, 5 h	 I + II (85) I:II = 10:7	32
 C ₂₇	(1.5)	<i>t</i> -BuOK (3), DME, rt, 5 h	 I + II (53) I:II = 10:9	32

^a Equivalents of base relative to TosMIC are given in brackets after the base.

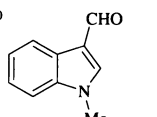
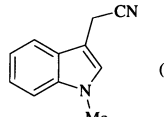
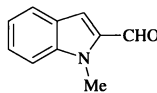
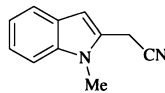
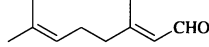
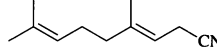
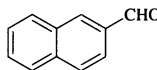
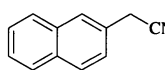
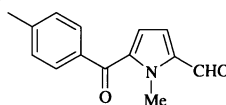
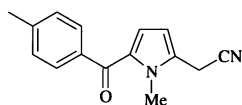
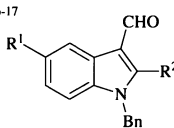
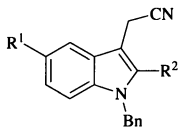
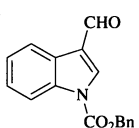
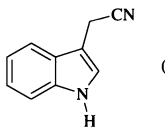
^b 9,10-Anthraquinone was formed in 31% yield.

TABLE IB. CYANIDES FROM ALDEHYDES BY REDUCTIVE CYANATION

Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.
C ₄ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -50°, 50 min 2. MeOH, reflux, 15 min	 (38)	62
C ₅ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -50°, 50 min 2. MeOH, reflux, 15 min	 (55)	62
	(1)	1. <i>t</i> -BuOK (2), THF, -20°, 30 min 2. MeOH, reflux, 15 min	 (81)	218
C ₆ 	(1.1)	1. <i>t</i> -BuOK (2), THF, -20°, 30 min 2. MeOH, reflux, 15 min	 (—)	65
	(1.1)	1. <i>t</i> -BuOK (2), DME, -45°, 30 min 2. MeOH, reflux, 15 min	" (76)	200
C ₆₋₇ 	(2.2)	1. <i>t</i> -BuOK (2), THF, -20°, 30 min 2. MeOH, reflux, 15 min	 $\frac{R}{H}$ (61) $\frac{Me}{Me}$ (73)	65
C ₇₋₈ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -50°, X min 2. MeOH, reflux, 15 min	 $\frac{R}{Cl}$ 10 (70) $\frac{X}{O_2N}$ 45 (10) $\frac{H}{H}$ 30 (67) $\frac{MeO}{MeO}$ 20 (70)	62
C ₉ 	(1)	1. <i>t</i> -BuOK, THF, -20°, 30 min 2. MeOH, reflux, 15 min	 (89)	64

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


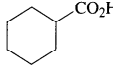
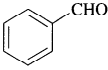
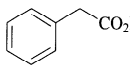
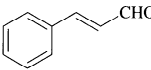
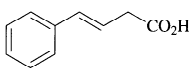
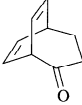
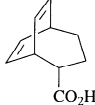
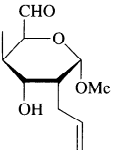
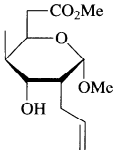
TABLE IB. CYANIDES FROM ALDEHYDES BY REDUCTIVE CYANATION (Continued)

Substrate	TosMIC (equiv.)	Conditions ^a	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -50° 2. MeOH, reflux	 (35)	219
	(1.1)	1. <i>t</i> -BuOK (2), DME, -50° 2. MeOH, reflux	 (48)	219
	(1.1)	1. <i>t</i> -BuOK (2), DME, -50°, 1 h 2. MeOH, reflux, 15 min	 (58)	62
C ₁₁ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -50°, 1 h 2. MeOH, reflux, 15 min	 (62)	62
C ₁₄ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -45°, 30 min 2. MeOH, reflux, 15 min	 (50)	200
C ₁₆₋₁₇ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -50° 2. MeOH, reflux	 $\frac{R^1}{H}$ $\frac{R^2}{H}$ (61) $\frac{Br}{H}$ (54) $\frac{Me}{Me}$ (69)	219
C ₁₇ 	(1.1)	1. <i>t</i> -BuOK (2), DME, -50° 2. MeOH, reflux	 (38)	219

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^a Equivalents of base relative to TosMIC are given in brackets after the base.

TABLE IC. CARBOXYLIC ACIDS AND ESTERS FROM KETONES OR ALDEHYDES VIA REDUCTIVE CYANATION

Substrate	Conditions ^a	Product(s) and Yield(s) (%)	Refs.
C ₃ 	1. TosMIC, <i>t</i> -BuOK (2), THF, -10°, 5 min 2. HCl (2 N), reflux, 10 h	 (62)	85
C ₅ <i>t</i> -BuCHO	1. TosMIC, <i>t</i> -BuOK (2), THF, -10°, 5 min 2. HCl (2 N), reflux, 10 h	<i>t</i> -BuCH ₂ CO ₂ H (60)	85
C ₆ 	1. TosMIC, <i>t</i> -BuOK (2), THF, -10°, 5 min 2. HCl (2 N), reflux, 10 h	 (55)	85
C ₇ 	1. PhSO ₂ CH ₂ N=C, <i>t</i> -BuOK (2), THF, -10°, 5 min 2. HCl (2 N), reflux, 10 h	 (65)	85
C ₉ 	1. TosMIC, <i>t</i> -BuOK (2), THF, -10°, 5 min 2. HCl (2 N), reflux, 1 h	 (67)	85
	1. TosMIC, <i>t</i> -BuOK (7), THF, <i>t</i> -BuOH, rt, 1 h 2. NaOH (2 N), reflux, 12 h	 (54)	185
C ₁₁ 	1. TosMIC, <i>t</i> -BuOK (2.2), THF, -10°, 8 min 2. HCl, MeOH, -10°, 2 h	 (35)	220

^a Equivalents of base relative to TosMIC are given in brackets after the base.

TABLE II. OXAZOLINES FROM KETONES OR ALDEHYDES


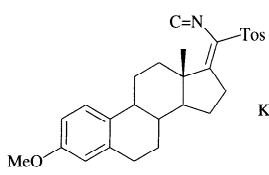
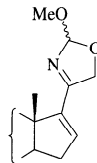
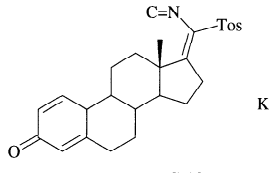
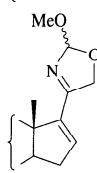
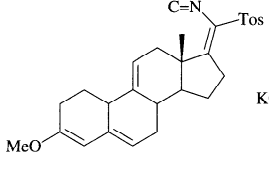
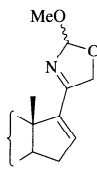
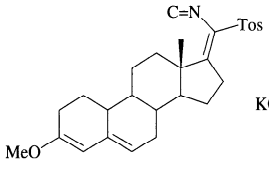
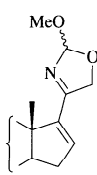
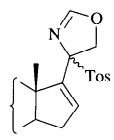
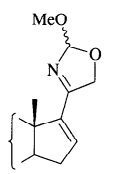
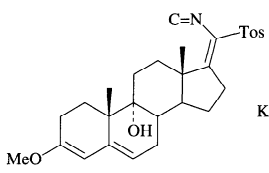
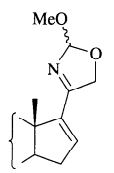
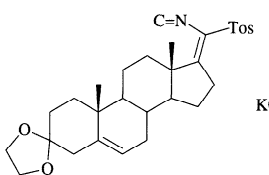
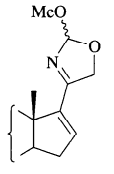
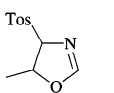
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ CH ₂ O	EtCH(Tos)N=C	<i>t</i> -BuOK, THF, rt, 2 h	 (81)	221
		KOH, THF, MeOH, rt, 1 h	 (90)	70
		KOH, THF, MeOH, rt, 1 h	 (81)	70
		KOH, THF, MeOH, rt, 1 h	 (91)	70
		KOH, THF, MeOH, rt, 1 h	 (96)	70
	"	NaOH (50%), BTEAC, C ₆ H ₆ , rt, 2 h	 (87)	70
	"	KOH, THF, rt, 3 min	" (95)	70
	"	NaOH (50%), BTEAC, C ₆ H ₆ , MeOH, rt, 2 h	 (90)	71, 70
	"	KOH, THF, MeOH, rt, 1 h	" (94)	70
		KOH, THF, MeOH, rt, 1 h	 (84)	70
		KOH, THF, MeOH, rt, 1 h	 (72)	70
C ₂ MeCHO	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, rt, 10 min	 (77)	26

TABLE II. OXAZOLINES FROM KETONES OR ALDEHYDES (Continued)

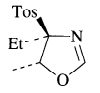
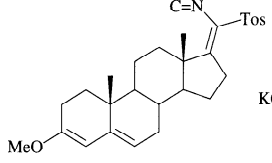
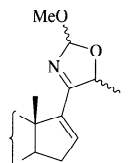
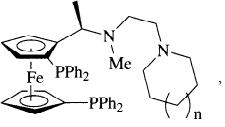
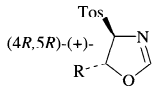

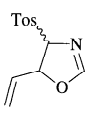







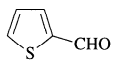
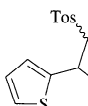
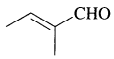
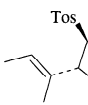

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.	
	$\text{EtCH}(\text{Tos})\text{N}=\text{C}$	<i>t</i> -BuOK, THF, rt, 2 h	 (>75)	221	
$\text{C}_{2,9}$		KOH, THF, MeOH, rt, 1 h	 mixture of diastereomers	70	
RCHO	$\text{TosCH}_2\text{N}=\text{C}$	 TfOAg (cat.), CH_2Cl_2 , rt, X h	 (4 <i>R</i> ,5 <i>R</i>)-(+)-	75	
	R	X	n = 1	n = 2	
	Me	2	(94) 83% ee	(93) 75% ee	
	(<i>E</i>)-MeCH=CH	9	(96) 85% ee	(95) 83% ee	
	<i>i</i> -Pr	2	(94) 86% ee	(91) 79% ee	
	<i>t</i> -Bu	7	(93) 80% ee	(97) 85% ee	
	4-ClC ₆ H ₄	1	(94) 73% ee	(94) 77% ee	
	Ph	2	(92) 77% ee	(96) 83% ee	
	4-MeOC ₆ H ₄	2	(96) 74% ee	(95) 77% ee	
	3,4-(MeO) ₂ C ₆ H ₃	2	(91) 80% ee	(97) 73% ee	
C_3		$\text{TosCH}_2\text{N}=\text{C}$	K_2CO_3 , MeOH, rt, 2.5 h	 (53)	26
		$\text{TosCH}_2\text{N}=\text{C}$	NaCN, EtOH, THF, 35°, 30 min	 (78)	36
		$\text{TosCH}_2\text{N}=\text{C}$	EtOTf, DME, EtOH, rt	 (60)	222
	EtCHO	$\text{TosCH}_2\text{N}=\text{C}$	NaCN, EtOH, rt, 25 min	 (92)	221
	$\text{EtCH}(\text{Tos})\text{N}=\text{C}$	<i>t</i> -BuOK, THF, rt, 2 h	 (>76)	221	
C_4		$\text{TosCH}_2\text{N}=\text{C}$	NaCN, EtOH, THF, 15°, 20 min	 (62)	36
C_5		$\text{TosCH}_2\text{N}=\text{C}$	NaH, DMSO, THF, rt, 72 h	 (59)	218
		$\text{TosCH}_2\text{N}=\text{C}$	NaCN, EtOH, rt, 25 min	 (85)	221
	<i>t</i> -BuCHO	$\text{TosCH}_2\text{N}=\text{C}$	NaCN, EtOH, rt, 25 min	 (87)	221

TABLE II. OXAZOLINES FROM KETONES OR ALDEHYDES (Continued)

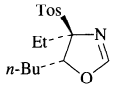
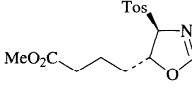

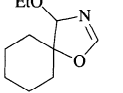
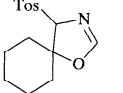

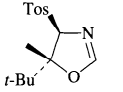
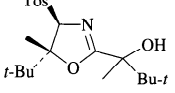
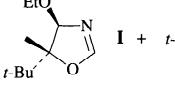
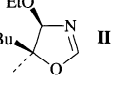
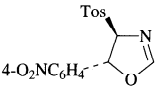
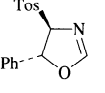
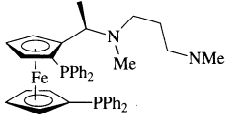
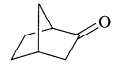
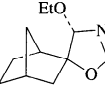
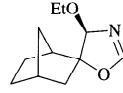
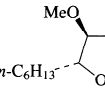
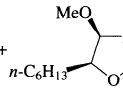
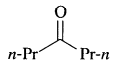
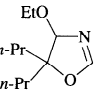
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>n</i> -BuCHO	EtCH(Tos)N=C	<i>t</i> -BuOK, THF, rt, 2 h	 (>75)	221
C ₆ MeO ₂ C(CH ₂) ₄ CHO	TosCH ₂ N=C	NaCN, EtOH, rt, 25 min	 (90)	221
	TosCH ₂ N=C	EtOTf, DME, EtOH, rt	 (72)	222
	TosCH ₂ N=C	KOH, DME, rt, 2 h	 (60)	77
	TosCH ₂ N=C	<i>t</i> -BuOLi, THF, -50°, 1 h	 (99)	55
	TosCH ₂ N=C	<i>n</i> -BuLi, THF, -50°, 1 h	 (99)	55
	TosCH ₂ N=C	EtOTf, DME, EtOH, rt	 I +  II I + II (35); I:II = 4:1	222
C ₇ 4-O ₂ NC ₆ H ₄ CHO	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, rt, 0.5 h	 (77)	223, 26
PhCHO	TosCH ₂ N=C	NaCN, EtOH, THF, 15°, 45 min	 I (94)	36
	TosCH ₂ N=C	NaCN, EtOH, rt, 25 min	I (92)	221
	TosCH ₂ N=C	 TfOAg (cat.), CH ₂ Cl ₂ , rt, 2 h	(4 <i>S</i> ,5 <i>S</i>)-(-)-I (96), 44% ee	75
	TosCH ₂ N=C	EtOTf, DME, EtOH, rt	 I +  II I + II (62); I:II = 4:1	222
<i>n</i> -C ₆ H ₁₃ CHO	TosCH ₂ N=C	NaOH, MeOH, rt, 2 h	 I +  II I + II (88); I:II = 7:1	31
	TosCH ₂ N=C	EtOTf, DME, EtOH, rt	 (75)	222

TABLE II. OXAZOLINES FROM KETONES OR ALDEHYDES (Continued)

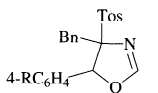


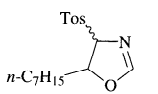
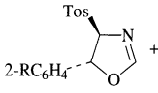
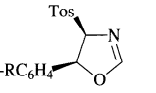
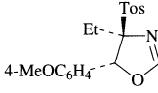
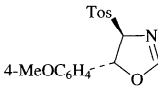

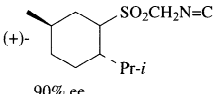
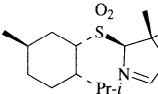
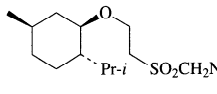
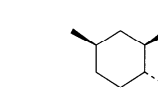
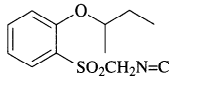
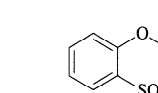
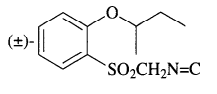
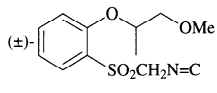
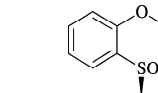
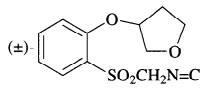
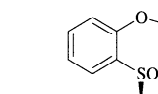
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇₋₈ 4-RC ₆ H ₄ CHO	BnCH ₂ CH(Tos)N=C	K ₂ CO ₃ , MeOH, rt, 5 min	  	69
C ₈ <i>n</i> -C ₇ H ₁₅ CHO	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, rt, 10 min		26
2-RC ₆ H ₄ CHO	TosCH ₂ N=C	K ₂ CO ₃ , MeOH	 	223
<u>R</u>			I + II (42); I:II = 1:2	
Me		0°, 6.5 h	I + II (73); I:II = 6:94	
Me		20°, 2 h	I + II (73); I:II = 6:94	
MeO		0°, 6 h	I + II (73); I:II = 7:3	
MeO		20°, 2 h	I + II (69); I:II = 9:11	
4-MeOC ₆ H ₄ CHO	EtCH(Tos)N=C	<i>t</i> -BuOK, THF, rt, 2 h		221
	TosCH ₂ N=C	NaCN, EtOH, rt, 25 min		221
	 90% ee	NaOH (50%), BTEAC, C ₆ H ₆ , 15°, 3 h	 (60) 18% de	40
	 (-), 100% ee	NaOH (50%), BTEAC, C ₆ H ₆ , 15°, 3 h	 (74) 33% de	40
	 (S)-(-), 50% ee	1. <i>n</i> -BuLi, THF, -60°, 2 h 2. -60 to 0°, 1 h	 I (76) 40% de	40
	 (±)	NaOH (50%), BTEAC, C ₆ H ₆ , 15°, 3 h	I (98) 40% de	40
	 (±)	NaOH (50%), BTEAC, PhMe, 15°, 3 h	 I (94) 20% de	40
	"	1. <i>n</i> -BuLi, THF, -60°, 2 h 2. -60 to 0°, 1 h	I (57) 33% de	40
	 (±)	NaOH (50%), BTEAC, C ₆ H ₆ , 15°, 3 h	 I (100) 7% de	40
	"	NaOH (50%), BTEAC, PhMe, 15°, 3 h	I (66) 20% de	40
	"	1. <i>n</i> -BuLi, THF, -60°, 2 h 2. -60 to 0°, 1 h	I (89) 40% de	40

TABLE II. OXAZOLINES FROM KETONES OR ALDEHYDES (Continued)





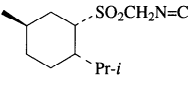

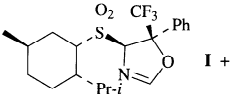
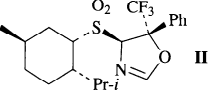
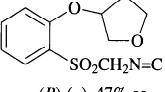

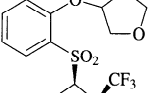
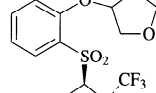
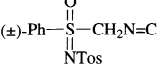


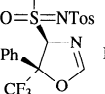
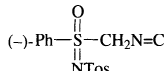
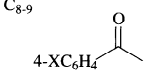
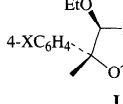
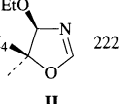
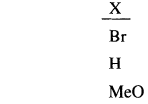
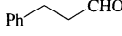
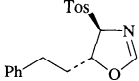
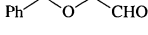
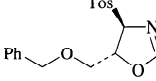
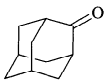
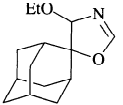
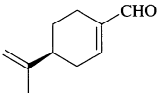
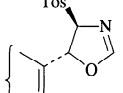
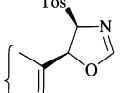
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH ₂ N=C	 , (EtO) ₄ Ti, CH ₂ Cl ₂ , 0°, 1 h	 I +  II I + II (100); I:II = 53:47	40
 (+) 90% ee		 , (EtO) ₄ Ti, CH ₂ Cl ₂ , 0°, 1 h	 I +  II I + II (96), 18% dc; I:II = 53:47	40
"		1. Triton B, THF, 20°, 4 h 2. CH ₂ Cl ₂ , 0°, 1 h	I + II (90), 18% dc; I:II = 66:34	40
 (R)-(-) 47% ee		 , (EtO) ₄ Ti, CH ₂ Cl ₂ , 0°, 1 h	 I +  II I + II (98), 41% dc; I:II = 60:40	40
 (±)-Ph-S(=O) ₂ -CH ₂ N=C		 , (EtO) ₄ Ti, CH ₂ Cl ₂ , 0°, 1 h	 I +  II I + II (100), 80% dc; I:II = 94:6	40
"		1. Triton B, THF, 20°, 4 h 2. CH ₂ Cl ₂ , 0°, 1 h	I + II (92), 80% dc; I:II = 95:5	40
 (-)-Ph-S(=O) ₂ -CH ₂ N=C 34% ee		1. Triton B, THF, 20°, 4 h 2. CH ₂ Cl ₂ , 0°, 1 h	I + II (91), 80% dc; I:II = 96:4	40
 C ₈₋₉ 4-XC ₆ H ₄ -C(=O)-R	TosCH ₂ N=C	EtOTf, DME, EtOH, rt	 I +  II I + II (55), I:II = 4:1 I + II (60), I:II = 4:1 I + II (40), I:II = 4:1	222
 C ₉				
 Ph-CH ₂ -CHO	TosCH ₂ N=C	NaCN, EtOH, rt, 25 min	 (91)	221
 Ph-CH ₂ -O-CH ₂ -CHO	TosCH ₂ N=C	NaCN, EtOH, rt, 25 min	 (88)	221
 C ₁₀	TosCH ₂ N=C	EtOTf, DME, EtOH, rt	 (92)	222
	TosCH ₂ N=C	NaCN, EtOH, rt, 25 min	 I +  II I + II (84), I:II = 1:1	221

TABLE II. OXAZOLINES FROM KETONES OR ALDEHYDES (Continued)

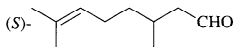
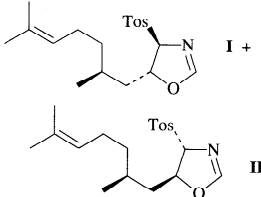
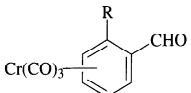
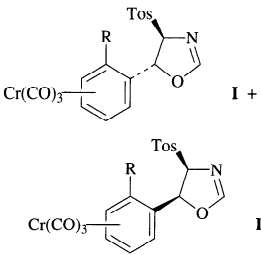
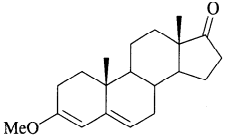
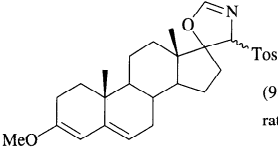
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH ₂ N=C	NaCN, EtOH, rt, 25 min	 I + II (83) I:II = 1:1	221
C ₁₁ 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, 0.5 h	 I + II	
R Me Me Me, (<i>R</i>)-(-) OMe OMe		0° 20° 0° 0° 20°	II (90) I + II (90); I:II = 2:1 (<i>a,R,4S,5R</i>)-(-)-I (95) I + II (90); I:II = 99:1 I + II (90); I:II = 17:3	223 223 74 223 223
C ₂₀ 	TosCH ₂ N=C	<i>t</i> -BuOLi, THF, -45°, 3 h	 (98) ratio 1:1	54

TABLE III-A. OXAZOLES FROM ALDEHYDES

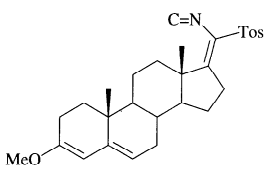
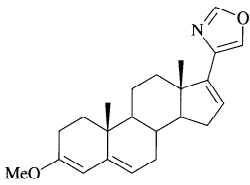
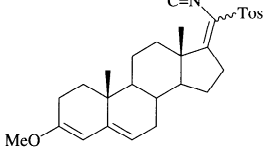
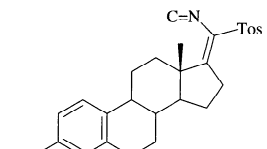
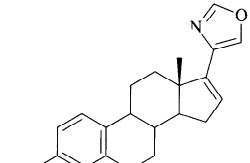
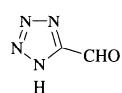
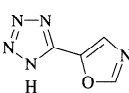
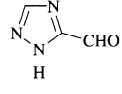
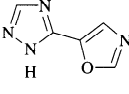
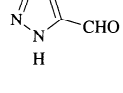
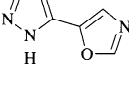
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ (CH ₂ O) _n		Na ₂ CO ₃ , MeOH, reflux, 5 h	 I (96)	70
		Na ₂ CO ₃ , MeOH, reflux, 7 h	I (94)	181
		Na ₂ CO ₃ , MeOH, reflux, 4 h	 (71)	181
C ₂ 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (87)	81
C ₃ 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (87)	81
C ₄ 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (44)	81

TABLE III-A. OXAZOLES FROM ALDEHYDES (Continued)

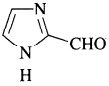
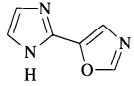
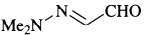
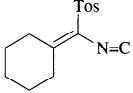
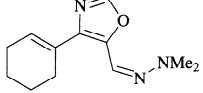
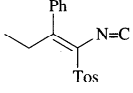
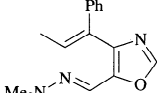

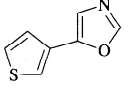
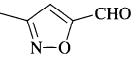
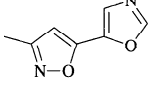
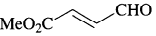
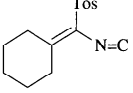
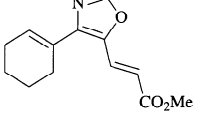
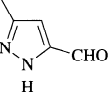
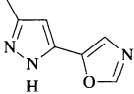
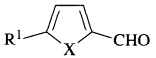
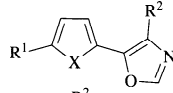

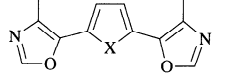
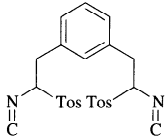
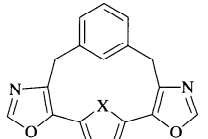
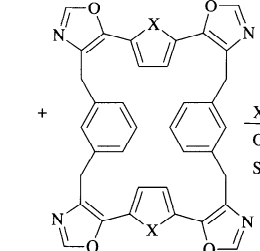
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (0) ^a	81
		<i>t</i> -BuOK, THF, -50° to rt, 1.5 h	 (75)	63
		1. <i>t</i> -BuOK, THF, 0° 2. rt, 4 h	 (80)	63
C ₅ 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 24 h	 (56)	218
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 1 h	 (65)	224
		<i>t</i> -BuOK, THF, -50° to rt, 1.5 h	 (71)	63
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (46)	81
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (0) ^b	78
X R ¹	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	H (81)	78
O H	MeCH(Tos)N=C	<i>t</i> -BuOK, MeOH, 40°, 20 min	Me (64)	69
O H	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 30 min	H (83)	78
O NO ₂	BnCH(Tos)N=C	K ₂ CO ₃ , MeOH, reflux, 30 min	Bn (62)	69
S H	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	H (79)	78
S H	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 24 h	H (77)	218
S H	BnCH(Tos)N=C	K ₂ CO ₃ , MeOH, reflux, 1 h	Bn (71)	69
S NO ₂	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 1 h	H (68)	78
C ₆ 	TosCH(Me)N=C	EtONa, EtOH, reflux, 2 h	 (48) S (76)	225 226
		EtONa, EtOH, reflux, 2 h	 (15) S (27)	225 226
			 (16) S (4)	225 226

TABLE III-A. OXAZOLES FROM ALDEHYDES (Continued)

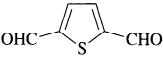
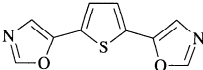
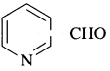
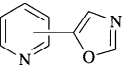
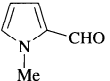
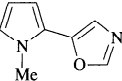
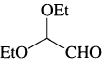
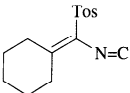
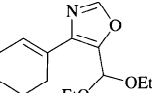

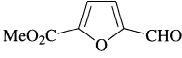
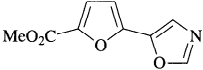
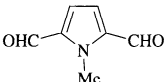
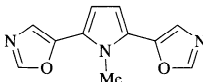

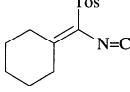
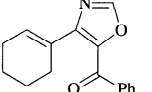
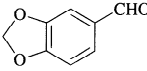
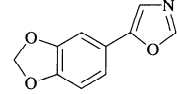
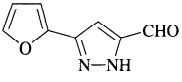
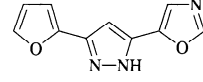
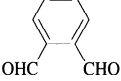
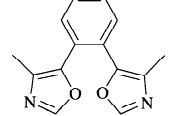
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 24 h	 (56)	218
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, X h	 (82)	78
<u>position</u>		<u>X</u>		
2		2	(82)	
3		3	(80)	
4		3	(67)	
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 3 h	 (47)	78
		<i>t</i> -BuOK, THF, -80° to rt, 2 h	 (91)	63
C ₇				
R ¹ CHO	TosCH(R ²)N=C		 (91)	
<u>R¹</u>	<u>R²</u>			
4-O ₂ NC ₆ H ₄	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(91)	26
4-ClC ₆ H ₄	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(57)	26
	Me	K ₂ CO ₃ , MeOH, reflux, 2 h	(74)	69
	Et	<i>t</i> -BuOK, MeOH, 40°	(73)	69
	Bn	K ₂ CO ₃ , MeOH, reflux, 2 h	(81)	69
<u>R¹</u>	<u>R²</u>			
Ph	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(91)	26
	Me	<i>t</i> -BuOK, MeOH, 40°, 20 min	(75)	69
	Me	K ₂ CO ₃ , MeOH, reflux, 1 h	(78)	73
	Et	K ₂ CO ₃ , MeOH, reflux, 1 h	(82)	69
<i>n</i> -C ₆ H ₁₃	H	KOH, MeOH, reflux, 4 days	(13)	31
	Me	KOH, Et ₂ O, rt, 3 h	(72)	31
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 3 h	 (88)	78
	TosCH ₂ N=C	Na ₂ CO ₃ , MeOH, reflux, 24 h	 (51)	65
C ₈				
		<i>t</i> -BuOK, THF, -70° to rt, 2 h	 (86)	63
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (90)	227
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (17)	81
	TosCH(Me)N=C	EtONa, EtOH, reflux, 2 h	 (57)	84

TABLE III-A. OXAZOLES FROM ALDEHYDES (Continued)

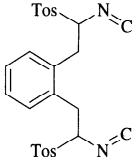
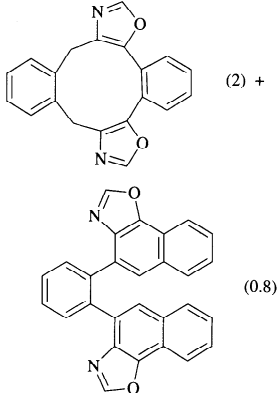
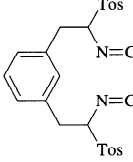
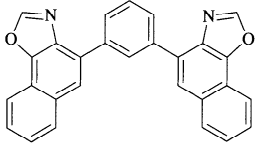
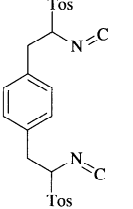
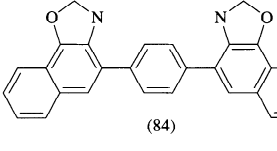
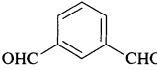
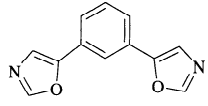
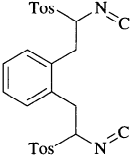
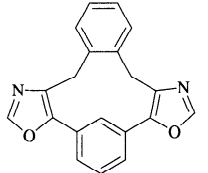
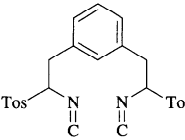
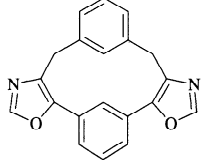
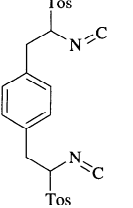
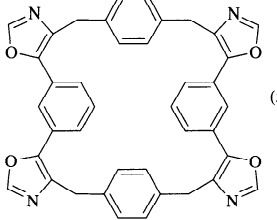
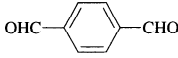
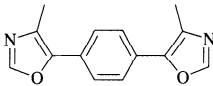
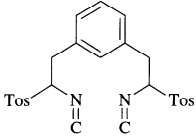
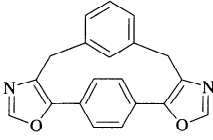
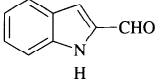
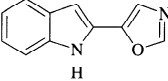
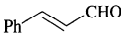
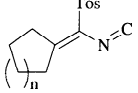
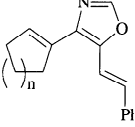
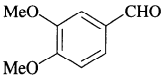
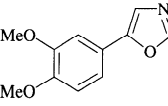
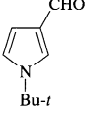
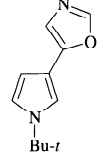
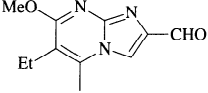
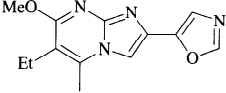
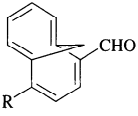
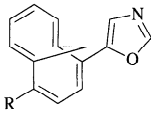
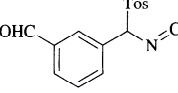
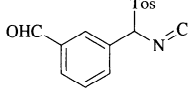
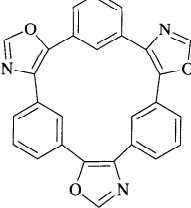
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		EtONa, EtOH, reflux, 2 h	 (2) + (0.8)	84
		EtONa, EtOH, reflux, 2 h	 (74)	84
		EtONa, EtOH, reflux, 2 h	 (84)	84
	TosCH(Me)N=C	EtONa, EtOH, reflux, 2 h	 (45)	84
		EtONa, EtOH, reflux, 2 h	 (84)	84
		EtONa, EtOH, reflux, 2 h	 (77)	84
		EtONa, EtOH, reflux, 2 h	 (52) + (15)	84

TABLE III-A. OXAZOLES FROM ALDEHYDES (Continued)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH(Me)N=C	EtONa, EtOH, reflux, 2 h	 (33)	84
		EtONa, EtOH, reflux, 2 h	 (85)	84
C_9 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (74)	81
		<i>t</i> -BuOK, THF, -78 to 20°, 2 h	 $\frac{n}{1}$ (90) $\frac{n}{2}$ (90)	80
	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 2 h	 (90)	227
	TosCH ₂ N=C	Na ₂ CO ₃ , MeOH, reflux, 24 h	 (62)	65
C_{11} 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 0.5 h	 (66)	228
C_{12-16} 	TosCH ₂ N=C	K ₂ CO ₃ , MeOH, reflux, 1 h	 (90) (92) (95)	229
C_{16} 		EtONa, EtOH, reflux, 3 h	 I (63)	82
	"	K ₂ CO ₃ , MeOH, reflux, 3 h	I (42)	82

^a See p. 440 (Eq. 46).^b 3-Tosylpyrrolo[1,2-c]pyrimidine was formed in ~20% yield instead of an oxazole.

TABLE III-B. TOSYLOXAZOLES FROM CARBOXYLIC ACID DERIVATIVES

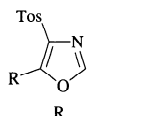
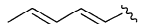

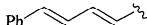
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
				
C ₄	TosCH ₂ N=C	KOH, DME, rt, 3 h	Me (66)	26
	TosCH ₂ N=C	<i>n</i> -BuLi, THF, -60 to 20°, 2 h	Me (73)	26
C ₇	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), THF, -70 to 0°, 2 h	 (25)	79
PhCOCl	TosCH ₂ N=C	KOH, DME, rt, 3 h	Ph (57)	26
	TosCH ₂ N=C	<i>n</i> -BuLi, THF, -60 to 20°, 2 h	Ph (65)	26
C ₈	TosCH ₂ N=C	KOH, DME, rt, 3 h	2-HO ₂ CC ₆ H ₄ (47)	26
PhCON=C=S	TosCH ₂ N=C	<i>n</i> -BuLi (1 eq), THF, -65°, 0.5 h; 0°, 2 h	Ph (70)	120
<i>n</i> -C ₆ H ₁₃ C(O)SeMe	TosCH ₂ N=C	DBU, Cu ₂ O, rt, 20 h	<i>n</i> -C ₆ H ₁₃ (40)	230
C ₉ PhCO ₂ Et	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), THF, -70 to 0°, 20 min	Ph (70)	79
	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), THF, -70 to 20°, 1.5 h	Ph (0)	79
C ₁₀	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), THF, -70 to 0°, 20 min	 (53)	79
C ₁₂	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), THF, -70 to 0°, 20 min	 (54)	79

TABLE IV. 1-FORMAMIDO-1-TOSYLALKENES FROM ALDEHYDES OR KETONES

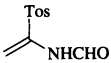
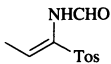

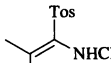
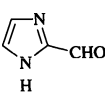
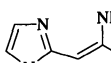
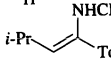
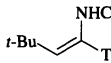
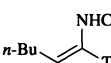

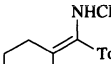
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ CH ₂ O	1. TosCH ₂ N=C, <i>t</i> -BuOK, DME, -60°, 1 h 2. AcOH	 (60)	86
C ₂ MeCHO	TosCH ₂ N=C, <i>t</i> -BuOK, THF, -70°, 15 min	 (41)	63
C ₃ 	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 (83)	36, 85
C ₄ 	TosCH ₂ N=C, K ₂ CO ₃ , MeOH, rt, 2 h	 (26)	81
<i>i</i> -PrCHO	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 (10)	36, 85
C ₅ <i>t</i> -BuCHO	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -30°, 30 min	 I (65)	86
	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	I (63)	36, 85
<i>n</i> -BuCHO	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -40°, 10 min	 (67)	136
C ₆ 	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 I (61)	36, 85
	TosCH ₂ N=C, <i>t</i> -BuOK, THF, -70 to -40°, 30 min	I (92)	63

TABLE IV. 1-FORMAMIDO-1-TOSYLALKENES FROM ALDEHYDES OR KETONES (Continued)


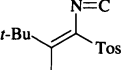
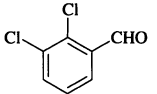
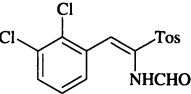
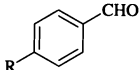
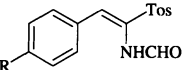
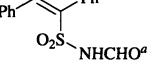

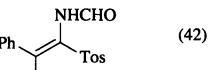
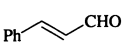
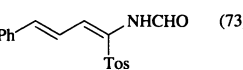

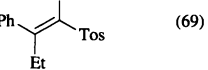
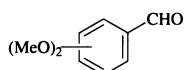
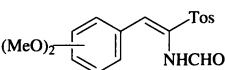
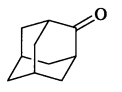
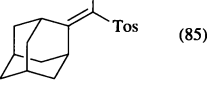
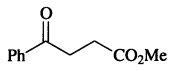
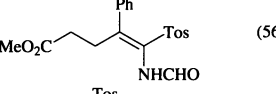
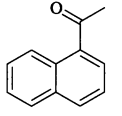
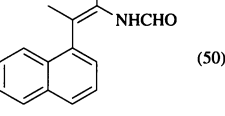

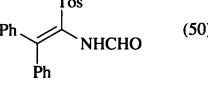
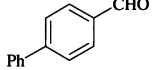
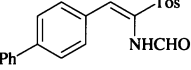
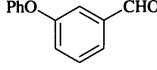
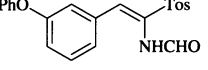
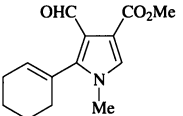
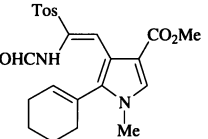
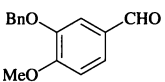
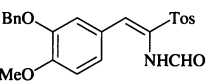
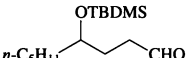
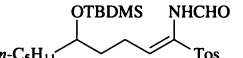
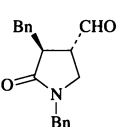
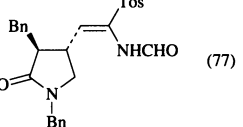
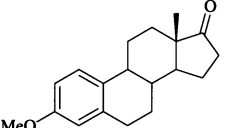
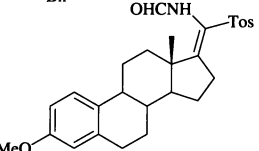
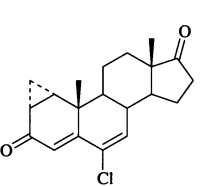
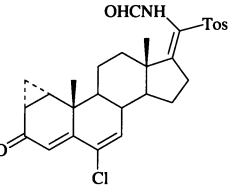
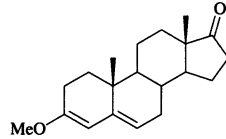
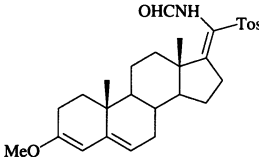
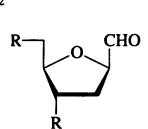
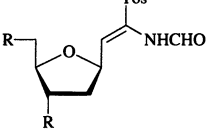
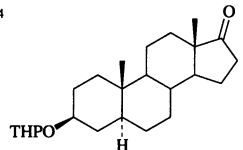
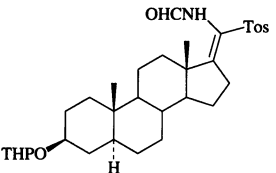
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -30°, 30 min	I (80)	86
	1. TosCH ₂ N=C, <i>t</i> -BuOLi, THF, -50°, 1 h 2. <i>t</i> -BuOK, THF, -50°, 10 min	 (71)	55
C₇ 	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -40°, 10 min	 (85)	136
	TosCH ₂ N=C, <i>t</i> -BuOK, DME		
$\frac{R}{Br}$	-30°, 30 min	(79)	114
$\frac{R}{NO_2}$	-60°, 1 h	(77)	86
$\frac{R}{H}$	-35°, 30 min	(87)	86
PhCHO	1. Ph-S(=O) ₂ -CH ₂ -N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 (73)	36, 85
C₈ 	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 (42)	36, 85
C₉ 	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 (73)	36, 85
	TosCH ₂ N=C, <i>t</i> -BuOK, THF, -70 to -40°, 30 min	 (69)	63
	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -20° 2. AcOH	 (80)	95, 231
$\frac{(MeO)_2}{3,4}$		(76)	
$\frac{(MeO)_2}{2,5}$			
C₁₀ 	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -30°, 30 min	 (85)	86
C₁₁ 	1. TosCH ₂ N=C, <i>t</i> -BuOLi, THF, -70 to -40°, 45 min 2. <i>t</i> -BuOK, -40°, 30 min	 (56)	63
C₁₂ 	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 (50)	36, 85
C₁₃ 	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -30°, 30 min	 (50)	86
	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -30°, 30 min	 (79)	114
	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -35°, 30 min	 (72)	232

TABLE IV. 1-FORMAMIDO-1-TOSYLALKENES FROM ALDEHYDES OR KETONES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄ 	TosCH ₂ N=C, <i>t</i> -BuOK, THF, -60°, 20 min	 (90)	63
C ₁₅ 	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -20° 2. AcOH	 (90)	96
	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -10°, 30 min	 (—)	233
C ₁₉ 	TosCH ₂ N=C, <i>t</i> -BuOK, DME	 (77)	234
	1. TosCH ₂ N=C, <i>t</i> -BuOLi, THF, -40°, 1.5 h 2. <i>t</i> -BuOK, -40°, 30 min	 (>94)	54
C ₂₀ 	TosCH ₂ N=C, <i>t</i> -BuOLi, THF, -75°, 5 h	 (29)	54
	TosCH ₂ N=C, <i>t</i> -BuOK, THF, -40°, 2 h	 (>85)	54
C ₂₂ 	TosCH ₂ N=C, <i>t</i> -BuOK, DME, -35°, 30 min	 (64) ^b	126
C ₂₄ 	1. TosCH ₂ N=C, <i>t</i> -BuOK, THF, -10°, 5 min 2. AcOH	 (73)	36

^a Phenylsulfonylmethyl isocyanide was used instead of TosMIC.

^b The tosyl group in Scheme 2 of ref. 128 is mistakenly depicted as TsO.

TABLE VA. 1-ISOCYANO-1-TOSYLALKENES BY DEHYDRATION OF 1-FORMAMIDO-1-TOSYLALKENES

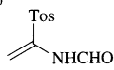

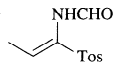

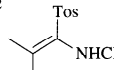

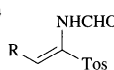

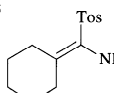

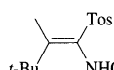


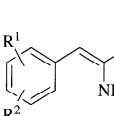
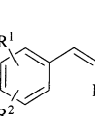
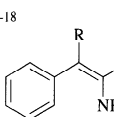
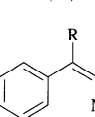
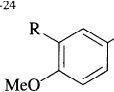

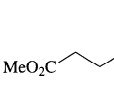

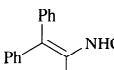

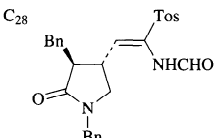
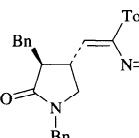
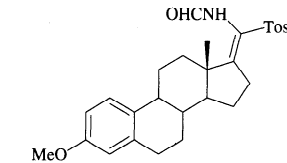
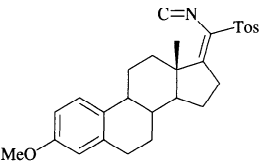
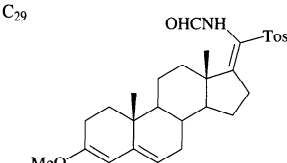
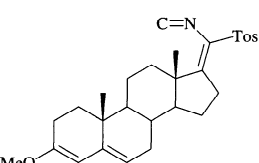
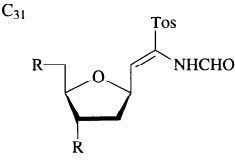
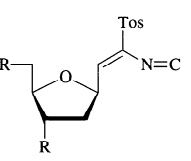
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	POCl ₃ , TEA, DME, -10°, 1.5 h	 (—) ^a	86
C ₁₁ 	POCl ₃ , DPA, THF, -35 to -20°, 30 min	 (—) ^b	63
C ₁₂ 	POCl ₃ , DPA, THF, -35 to -20°, 30 min	 (89)	63, 86
C ₁₄ 	POCl ₃ , TEA, DME, 0°, 1 h	 (77)	86
	THF, -30°, 10 min	(50)	136
C ₁₅ 	POCl ₃ , DPA, THF, -35 to -20°, 30 min	 (90)	63
	POCl ₃ , TEA, THF, 0°, 45 min	 (70)	55
	POCl ₃ , TEA, DME, 0°, 1 h, chromatography, Al ₂ O ₃	 (64)	55
C ₁₆ 	POCl ₃ , TEA, DME, -20°, 1 h	 (52)	136
	0°, 1 h	(—)	114
	0°, 0.5 h	(55)	86
	0°, 1 h	(54)	86
C ₁₇₋₁₈ 	POCl ₃ , DPA, THF, -35 to -20°, 30 min	 (49)	63
		(89)	
C ₁₈₋₂₄ 	POCl ₃ , TEA, CH ₂ Cl ₂ , rt, 17 h	 (80)	95
		(90)	96
C ₂₀ 	POCl ₃ , DPA, THF, -35 to -20°, 30 min	 (—) ^{a,b}	63
C ₂₂ 	POCl ₃ , TEA, DME, 0°, 1 h	 (68)	86

TABLE VA. 1-ISOCYANO-1-TOSYLALKENES BY DEHYDRATION OF 1-FORMAMIDO-1-TOSYLALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₈	POCl ₃ , TEA	 (94) ^a	234
 C ₂₉	POCl ₃ , DPA, THF, 0°, 1 h	 (94)	54
 C ₂₉	POCl ₃ , DPA, THF, 0°, 1 h	 (85)	54
 C ₃₁	POCl ₃ , TEA, DME, -5°, 1 h	 (42) ^c	126

R = 4-MeC₆H₄CO₂^a The product, an unstable oil, was converted directly to the imidazole^b The isocyanide was not isolated but was used in solution, owing to its instability.^c The tosyl group in Scheme 2 of ref 128 is mistakenly depicted as TsO.

TABLE VB. 1-ISOCYANO-1-TOSYLALKENES BY IN SITU DEHYDRATION OF 1-FORMAMIDO-1-TOSYLALKENES


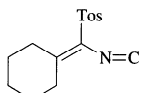
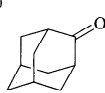
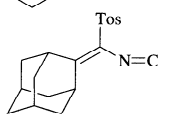
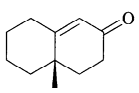
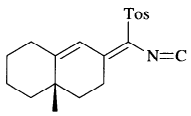
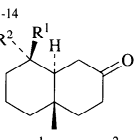
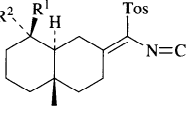
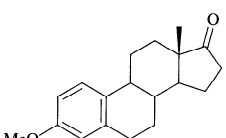
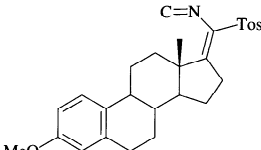
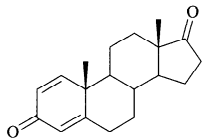
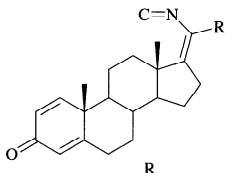
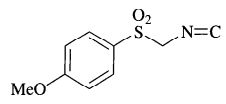
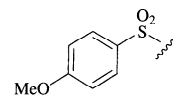
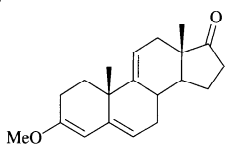
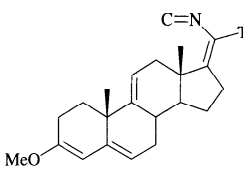
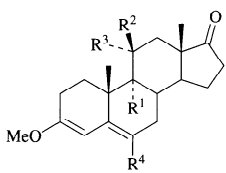
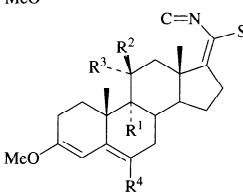
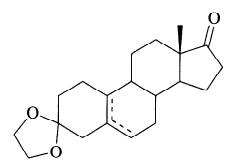
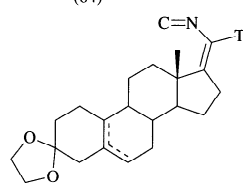
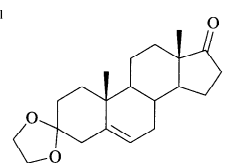
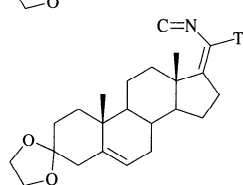
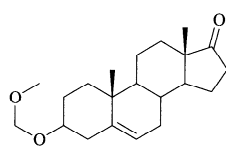
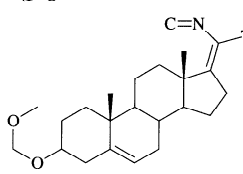
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₆ 	TosCH ₂ N=C	1. <i>t</i> -BuOK, DME, -30°, 0.5 h 2. AcOH 3. POCl ₃ , TEA, 0°, 1 h	 (58)	86												
C ₁₀ 	TosCH ₂ N=C	1. <i>t</i> -BuOK, DME, -30°, 0.5 h 2. AcOH 3. POCl ₃ , TEA, 0°, 1 h	 (64)	86												
C ₁₁ 	TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -45°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1.5 h	 (86)	235												
C ₁₁₋₁₄ 	TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -45°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1.5 h		235												
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>OH</td> <td>H</td> </tr> <tr> <td>OH</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>OH</td> </tr> <tr> <td>OTMS</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	H	H	OH	H	OH	Me	Me	OH	OTMS	H	
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			(91) <i>E:Z</i> = 1:1 (99) <i>E:Z</i> = 2.5:1 (98) <i>E:Z</i> = 1:1 (97) <i>E:Z</i> = 1:1 (92) <i>E:Z</i> = 2:1													
C ₁₉ 	TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -45°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1.5 h	 (70)	54												

TABLE VB. 1-ISOCYANO-1-TOSYLALKENES BY IN SITU DEHYDRATION OF 1-FORMAMIDO-1-TOSYLALKENES (Continued)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																		
	TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -45°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1.5 h		54																																																																																		
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	TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -45°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1.5 h		(77) 54																																																																																		
	R ⁵ SO ₂ CH ₂ N=C	1. <i>t</i> -BuOK, THF, -45°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA		54																																																																																		
	<table border="1" data-bbox="321 998 512 1113"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	H	H	H	H	H	H	H	H	H	H	H	H	<table border="1" data-bbox="598 998 841 1113"> <thead> <tr> <th>R⁵</th> </tr> </thead> <tbody> <tr> <td>Me</td> </tr> <tr> <td><i>t</i>-Bu</td> </tr> <tr> <td>Ph</td> </tr> </tbody> </table>	R ⁵	Me	<i>t</i> -Bu	Ph	<table border="1" data-bbox="841 998 946 1113"> <thead> <tr> <th>POCl₃, TEA</th> </tr> </thead> <tbody> <tr> <td>0°, 1.5 h</td> </tr> <tr> <td>0°, 1.5 h</td> </tr> <tr> <td>0°, 1.5 h</td> </tr> </tbody> </table>	POCl ₃ , TEA	0°, 1.5 h	0°, 1.5 h	0°, 1.5 h	<table border="1" data-bbox="1189 1021 1223 1113"> <tbody> <tr> <td>(84)</td> </tr> <tr> <td>(4)</td> </tr> <tr> <td>(67)</td> </tr> </tbody> </table>	(84)	(4)	(67)																																																							
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		TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -40°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1 h		(81) 54																																																																																	
		TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -40°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1 h		(70) 54																																																																																	

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TABLE VB. 1-ISOCYANO-1-TOSYLALKENES BY IN SITU DEHYDRATION OF 1-FORMAMIDO-1-TOSYLALKENES (Continued)

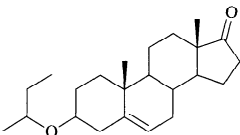
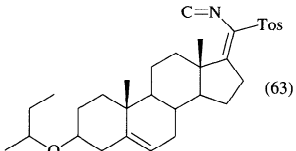
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₃ 	TosCH ₂ N=C	1. <i>t</i> -BuOK, THF, -40°, 2 h 2. H ₃ PO ₃ 3. POCl ₃ , TEA, 0°, 1 h	 (63) 54	

TABLE VC. 1-ISOCYANO-1-TOSYLALKENES FROM ALDEHYDES OR KETONES BY PETERSON OLEFINATION


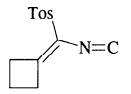
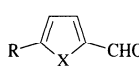
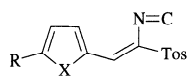
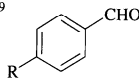
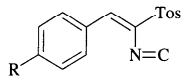
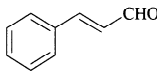
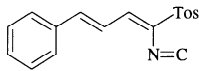
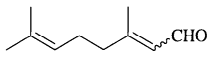
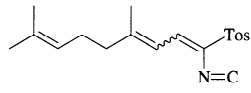
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 	TosC(Li)(TMS)N=C	THF, -60°, 10 min	 (64)	87
C ₅ 	TosC(Li)(TMS)N=C	THF,		87
		-80°, 10 min	(10)	
		-80 to -30°, 1 h	(88)	
		-70°, 10 min	(87)	
C ₇₋₉ 	TosC(Li)(TMS)N=C	THF, -80 to -30°, 1 h		87
			(85)	
			(55)	
			(82)	
			(93)	
			(76)	
C ₉ 	TosC(Li)(TMS)N=C	THF, -95°, 0.5 h	 I (83)	87
	TosC(Li)(TMS)N=C	THF, -80 to -30°, 30 min	I (>73)	34
C ₁₀ 	TosC(Li)(TMS)N=C	THF, -95°, 0.5 h	 (90)	87

TABLE VI. MONOALKYLATION OF TOSMIC


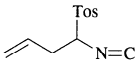
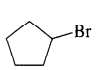
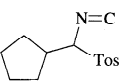
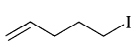
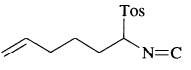
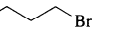
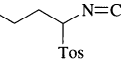
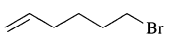
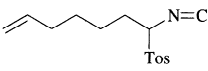
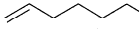

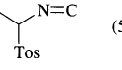
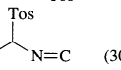
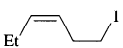
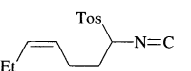
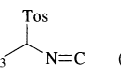
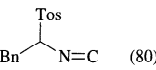
Substrate (equiv)	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ MeI (2)	NaOH (30%), BTEAC, CH ₂ Cl ₂ , 0°, 3 h	MeCH(Tos)N=C (95) ^a	90, 73
C ₂ EtBr (2)	NaOH (30%), TBAI, CH ₂ Cl ₂ , 0°, 2 h	EtCH(Tos)N=C (80) ^a	90
EtI (2)	NaOH (30%), TBAI, CH ₂ Cl ₂ , 0°, 2 h	EtCH(Tos)N=C (90) ^a	90
C ₃  (2)	NaOH (30%), TBAI, CH ₂ Cl ₂ , 0°, 1.5 h	 I (75)	90
(1.9)	NaOH (30%), BTEAC, CH ₂ Cl ₂ , 0°, 4 h	I (91)	91
<i>i</i> -PrBr (1.2)	NaH, DMSO, Et ₂ O, rt, 1 h	<i>i</i> -PrCH(Tos)N=C I (71)	73
<i>i</i> -PrCl (10)	NaOH (30%), TBAI, CH ₂ Cl ₂ , 5°, 80 h	I (40)	90
<i>i</i> -PrI (10)	NaOH (40%), TBAI, CH ₂ Cl ₂ , 6°, 80 h	I (42)	73
<i>n</i> -PrI (2)	NaOH (30%), TBAI, CH ₂ Cl ₂ , 20°, 4 h	<i>n</i> -PrCH(Tos)N=C (85)	90
C ₄ <i>s</i> -BuBr (1.2)	NaH, DMSO, Et ₂ O, rt, 1 h	<i>s</i> -BuCH(Tos)N=C (65)	73
<i>t</i> -BuBr (3)	NaH, DMSO, Et ₂ O, rt, 1 h	<i>t</i> -BuCH(Tos)N=C (0) ^b	73
<i>t</i> -BuI (3)	NaH, DMSO, Et ₂ O, rt, 1 h	<i>t</i> -BuCH(Tos)N=C (0) ^b	73
<i>n</i> -BuI (2)	NaOH (30%), TBAI, CH ₂ Cl ₂ , 25°, 4 h	<i>n</i> -BuCH(Tos)N=C (75)	90
TMSCH ₂ I (1.2)	NaOH (50%), TBAI, THF, rt, 1.5 h	TMSCH ₂ CH(Tos)N=C I (85)	93
(1.9)	NaOH (30%), BTEAC, CH ₂ Cl ₂ , 0°, 4 h	I (51)	91
C ₅  (1.05)	NaH, DMSO, Et ₂ O, rt, 2 h	 (58)	73
 (1.1)	NaOH (40%), TBAI, CH ₂ Cl ₂ , rt, 5 h	 (78)	63
MeO ₂ C-  Br (1)	NaOH (25%), THAI, CH ₂ Cl ₂ , rt, 18 h	MeO ₂ C-  N=C (50)	160
C ₆  (→)	LDA, THF	 I (73)	163
 (1.1)	NaOH (40%), TBAI, CH ₂ Cl ₂ , rt, 14 h	I (83)	63
<i>t</i> -BuO ₂ C-  Br (1.9)	NaOH (30%), BTEAC, CH ₂ Cl ₂ , 0°, 4 h	<i>t</i> -BuO ₂ C-  N=C (51)	91
C ₆ H ₁₁ I (3)	NaH, DMSO, Et ₂ O, rt, 2 h	C ₆ H ₁₁ -  N=C (30)	73
Et-  I (1.1)	1. NaOH (30%), TBAB, CH ₂ Cl ₂ , 0°, 3 h 2. rt, 6 h	Et-  N=C (80)	152
<i>n</i> -C ₆ H ₁₃ I (1.1)	1. NaOH (30%), TBAB, CH ₂ Cl ₂ , 0°, 3 h 2. rt, 6 h	<i>n</i> -C ₆ H ₁₃ -  N=C (80)	152
C ₇ BnBr (2)	NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 1.5 h	Bn-  N=C (80)	73, 90

TABLE VI. MONOALKYLATION OF TOSMIC (Continued)

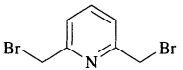
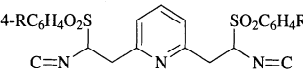
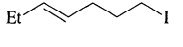
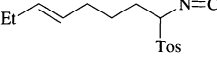
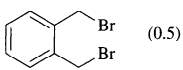
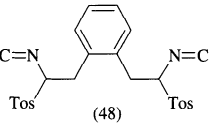
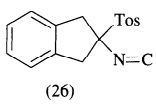
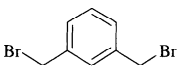
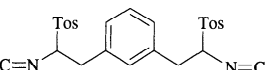

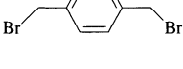
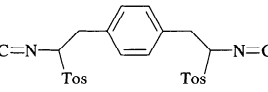

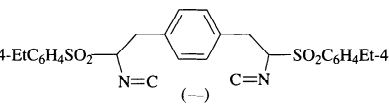
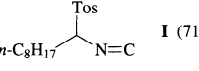
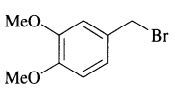
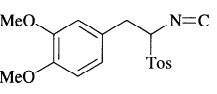
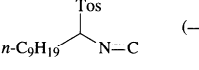
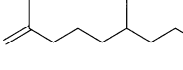
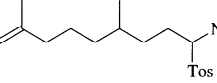
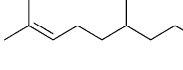
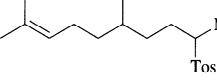
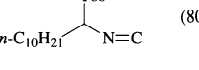
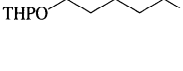
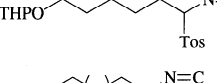
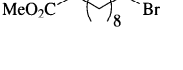
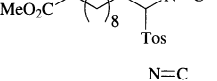
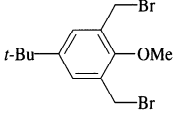
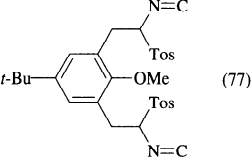
Substrate (equiv)	Conditions	Product(s) and Yield(s) (%)	Refs.
 (0.8)	NaOH (20%), TBAI, CH ₂ Cl ₂ , rt, 2 h, 4-RC ₆ H ₄ SO ₂ CH ₂ N=C instead of TosMIC	 $\frac{R}{Et}$ Et (—) 92 EtO (—)	92
Et-  (1)	NaOH (30%), <i>n</i> -Bu ₄ NOH, CH ₂ Cl ₂ , 0°, 4 h	 (70)	97
C ₈  (0.5)	NaOH (7.5 N), TBAI, CH ₂ Cl ₂ , 5°, 4 h	 (48) +  (26)	153
 (0.5)	NaOH (7.5 N), TBAI, CH ₂ Cl ₂ , 5°, 4 h	 I (70)	153
 (0.5)	NaOH (20%), TBAI, CH ₂ Cl ₂ , rt, 2 h	I (76)	92
 (0.5)	NaOH (7.5 N), TBAI, CH ₂ Cl ₂ , 5°, 4 h	 (67)	153
 (0.5)	NaOH (20%), TBAI, CH ₂ Cl ₂ , rt, 2 h, 4-EtC ₆ H ₄ SO ₂ CH ₂ N=C instead of TosMIC	 (—)	92
<i>n</i> -C ₈ H ₁₇ Br (1.2)	NaH, DMSO, Et ₂ O, rt, 2 h	 I (71)	73
<i>n</i> -C ₈ H ₁₇ I (1)	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 1 h; rt, 12 h	I (80)	237
C ₉  (1)	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 2 h; rt, 12 h	 (85)	105
<i>n</i> -C ₉ H ₁₉ I (1)	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 2 h; rt, 12 h	 (—)	237, 105
C ₁₀  (1.1)	NaOH (40%), TBAI, CH ₂ Cl ₂ , rt, 4 h	 (75)	238
 (1.1)	Alkali, TBAI, CH ₂ Cl ₂ , rt	 (75)	239
<i>n</i> -C ₁₀ H ₂₁ I (1)	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 2 h; rt, 12 h	 (80)	240, 105
THPO-  (1)	NaOH (40%), TBAB, CH ₂ Cl ₂ , rt	THPO-  (92)	151
C ₁₂ MeO ₂ C-  (1)	NaOH (25%), TBAI, CH ₂ Cl ₂ , rt, 18 h	MeO ₂ C-  (28)	160
C ₁₃  (0.25)	NaOH (20%), TBAI, CH ₂ Cl ₂ , rt, 2 h	 (77)	156

TABLE VI. MONOALKYLATION OF TOSMIC (Continued)

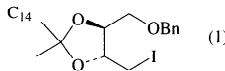
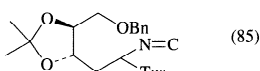
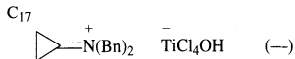
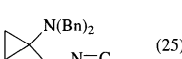
Substrate (equiv)	Conditions	Product(s) and Yield(s) (%)	Refs.
THPO $(\text{---})_6\text{I}$ (1)	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 3 h; rt, 6 h	THPO $(\text{---})_6\text{N}=\text{C}$ Tos (80)	152
$n\text{-C}_8\text{H}_{17}\text{---}\equiv\text{---}\text{I}$ (—)	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 2 h; rt, 12 h	$n\text{-C}_8\text{H}_{17}\text{---}\equiv\text{---}\text{N}=\text{C}$ Tos (78)	105
 (1)	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 2 h; rt, 12 h	 (85)	105
 (—)	LDA, THF, CH ₂ Cl ₂ , -78°, 1 h	 (25)	241
MeO ₂ C $(\text{---})_{13}\text{Br}$ (1)	NaOH (25%), THAI, CH ₂ Cl ₂ , rt, 18 h	MeO ₂ C $(\text{---})_{13}\text{N}=\text{C}$ Tos (20)	160
$n\text{-C}_{18}\text{H}_{37}\text{X}$ (1)	NaOH (40%), <i>n</i> -Bu ₄ NOH, CH ₂ Cl ₂ , 0°, 12 h	$n\text{-C}_{18}\text{H}_{37}\text{N}=\text{C}$ Tos (65) I (85)	242
$n\text{-C}_{19}\text{H}_{39}\text{I}$ (1)	NaOH (40%), <i>n</i> -Bu ₄ NOH, CH ₂ Cl ₂ , rt, ~16 h	$n\text{-C}_{19}\text{H}_{39}\text{N}=\text{C}$ Tos (19)	243
$n\text{-C}_5\text{H}_{11}\text{---}(\text{---})_4\text{---}\text{Br}$ (1)	NaOH (25%), THAI, CH ₂ Cl ₂ , rt, 18 h	$n\text{-C}_5\text{H}_{11}\text{---}(\text{---})_4\text{---}\text{N}=\text{C}$ Tos (34)	160
$n\text{-C}_8\text{H}_{17}\text{---}(\text{---})_7\text{---}\text{Br}$	NaOH (25%), THAI, CH ₂ Cl ₂ , rt, 18 h	$n\text{-C}_8\text{H}_{17}\text{---}(\text{---})_7\text{---}\text{N}=\text{C}$ Tos (33)	160

TABLE VI. MONOALKYLATION OF TOSMIC (Continued)

Substrate (equiv)	Conditions	Product(s) and Yield(s) (%)	Refs.
$n\text{-C}_8\text{H}_{17}\text{---}(\text{---})_9\text{---}\text{Br}$	NaOH (25%), THAI, CH ₂ Cl ₂ , rt, 18 h	$n\text{-C}_8\text{H}_{17}\text{---}(\text{---})_9\text{---}\text{N}=\text{C}$ Tos (33)	160
$n\text{-C}_8\text{H}_{17}\text{---}(\text{---})_9\text{---}\text{I}$	NaOH (40%), TBAB, CH ₂ Cl ₂ , 0°, 2 h; rt, 12 h	$n\text{-C}_8\text{H}_{17}\text{---}(\text{---})_9\text{---}\text{N}=\text{C}$ Tos (75)	105

^a This compound has also been prepared by the Mannich approach (Eq. 16).

^b This compound has been obtained by a different method: see Eqs. 59 and 60.

TABLE VIII. DISUBSTITUTED DERIVATIVES OF TOSMIC


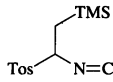
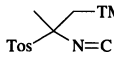
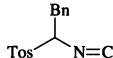
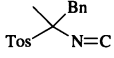
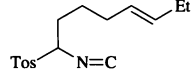
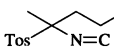
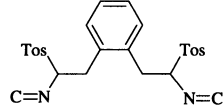
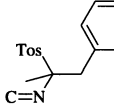
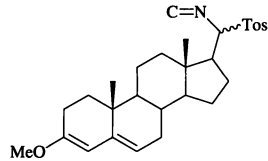
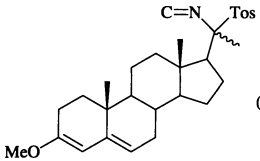
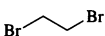
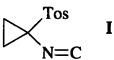
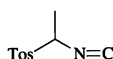
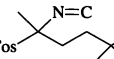
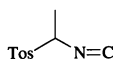
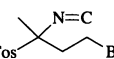
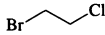
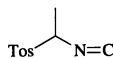
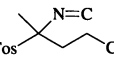
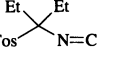
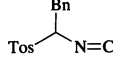
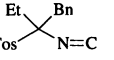
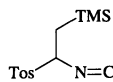
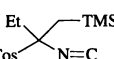
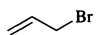
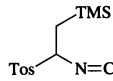
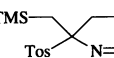
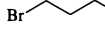
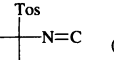
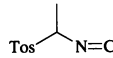
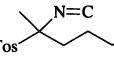
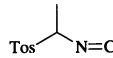
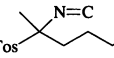
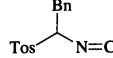
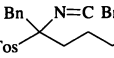
Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.		
C ₁	MeI (2)	TosCH ₂ N=C	<i>n</i> -BuLi, THF, -70 to 0°, 0.5 h	 I (90)	79	
	(2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 0.5 h	I (90)	244	
	(13)		<i>t</i> -BuOK, THF, -5° to rt, 1 h	 (92)	93	
	(1.1)		NaOH (40%), TBAI, CH ₂ Cl ₂ , rt, 2 h	 (71)	73	
	(1.5)		NaH, DMSO, Et ₂ O	 (95)	97	
	(2)		NaH, DMSO, rt, 3 h	 (26)	83	
	(8)		NaOH (50%), BTEAC, PhMe, 80°, 30 min	 (100)	45	
	C ₂	 (1.2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 1.5 h	 I (81)	73
(—)		TosCH ₂ N=C	NaH, HMPA, THF, 0°	I (80)	99	
(—)			NaH, DMSO, Et ₂ O, 35°, 1 h	 (18)	100	
(4)			NaH, DMSO, Et ₂ O, 35°, 1 h	 (42)	100	
 (1.4)			NaH, DMSO, Et ₂ O, 35°, 1 h	 (81)	100	
EtI (2)		TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20 to 35°, 2 h	 (80)	35	
(1.2)			NaH, DMSO, Et ₂ O, rt, 1 h	 (84)	73	
(6.5)			<i>t</i> -BuOK, THF, -5° to rt, 3 h	 (81)	93	
C ₃		 (10)		<i>t</i> -BuOK, THF, 0°, 2 h	 (79)	93
		 (1.2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 1 h	 (71)	148
	(0.5)		NaH, DMSO, Et ₂ O, 35°, 1 h	 (91)	100	
	(5)		NaH, DMSO, Et ₂ O, 35°, 1 h	 (53)	100	
	(0.5)		NaH, DMSO, Et ₂ O, 35°, 1 h	 (70)	100	

TABLE VIIA. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

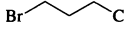
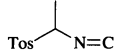
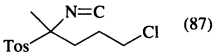
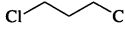
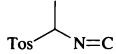
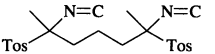
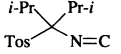
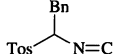
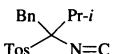
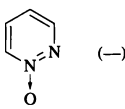
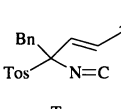
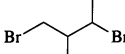
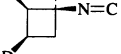
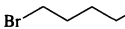

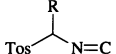
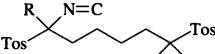
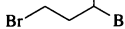
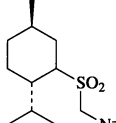
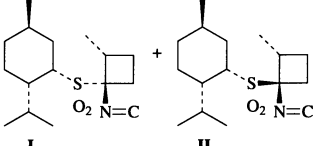
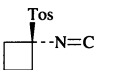
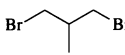
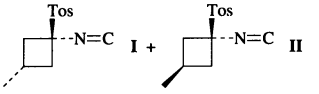
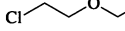
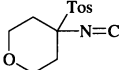
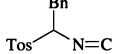
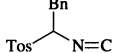
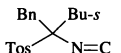
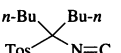
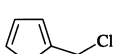
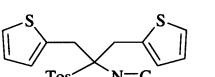
Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
 (1.5)		NaH, DMSO, Et ₂ O, 35°, 1 h	 (87)	100
 (0.5)		NaH, DMSO, Et ₂ O, 35°, 1 h	 (35)	100
<i>i</i> -PrI (2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 1 h	 (>47)	98
(1.1)		NaH, DMSO, Et ₂ O, rt, 1 h	 (>65)	98
C ₄  (—)	TosCH ₂ N=C	1. <i>n</i> -BuLi (2 eq), THF, -70 to 0°, 2 h 2. BnBr, 0°, 1 h	 (52)	79
 (—)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt	 (52)	245
 (1)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 1.5 h	 (70)	73
X-CH ₂ -CH ₂ -CH ₂ -X (0.5)		NaH, DMSO, Et ₂ O,		100
X	R			
Br	Me	35°, 1 h	(89)	
I	Me	35°, 1 h	(94)	
Br	Ph	20-35°, 1 h	(17)	
I	Ph	20-35°, 1 h	(87)	
Br	Bn	20-35°, 1 h	(76)	
 (1)		NaH, DMSO, Et ₂ O, rt, 1.5 h	 I + II (99); I:II = 1:1	39
(1.2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-35°, 1 h	 (65)	148
 (1.2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt	 I + II (74); I:II = 2.7:1	148
 (3)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-40°, 3 h	 (39)	73
<i>s</i> -BuBr (—)		NaH, DMSO, Et ₂ O, rt, 1 h	No reaction	73
<i>s</i> -BuI (1.2)		NaH, DMSO, Et ₂ O, rt, 1 h	 (56)	73
<i>n</i> -BuI (2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-35°, 2 h	 (>69)	98
C ₅  (2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-35°, 2 h	 (—)	246

TABLE VIIA. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

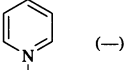
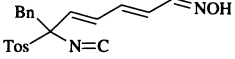
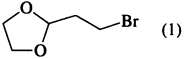
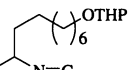
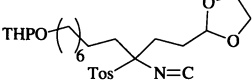

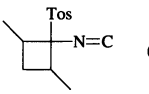
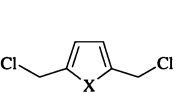
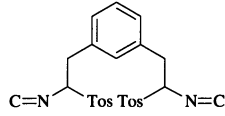
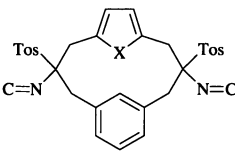
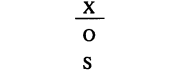
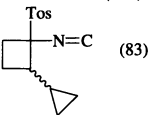
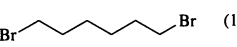
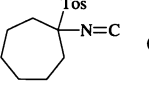

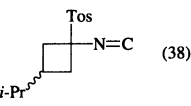
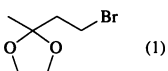

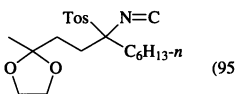

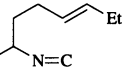
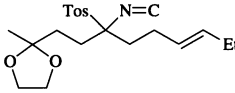
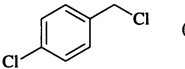
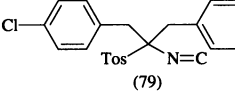
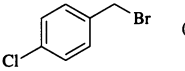
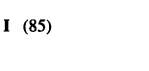
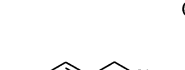

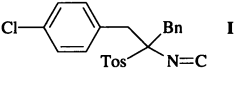
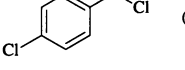

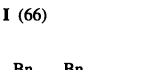

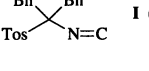

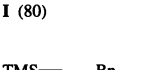


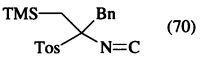


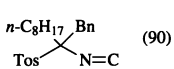
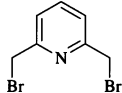
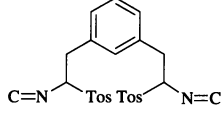
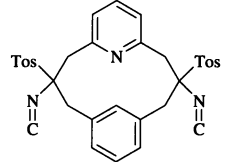
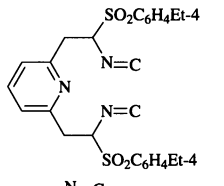
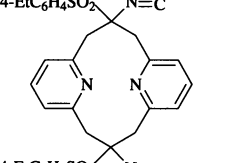
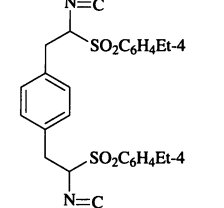
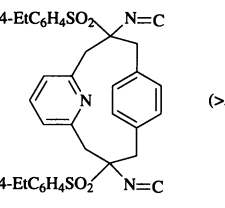
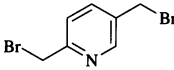
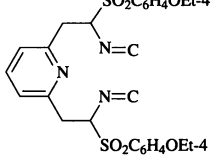
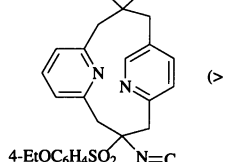
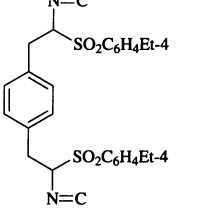
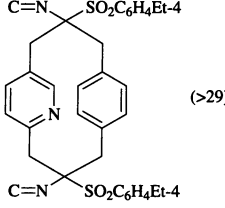
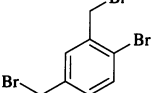
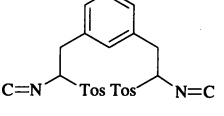
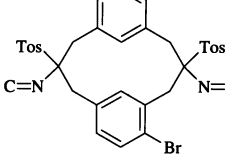
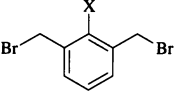
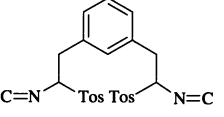
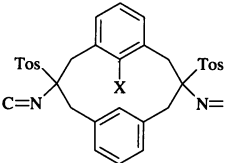
Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
 (—)	TosCH ₂ N=C	1. <i>n</i> -BuLi (2 eq), THF, -70 to 0°, 2 h 2. BnBr, 0°, 1 h	 (64)	79
 (1)	Tos-  N=C	NaH, DMSO, Et ₂ O, 15°, 3 h	 (>75)	152
 (1.2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt	 (>20)	247
 (1.1)		sl. add. to NaOH (Y%), TBAI, CH ₂ Cl ₂ , reflux, t h	 (>39) (>41)	92
 (1.2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 45 min	 (83)	247
 (1)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 1 h	 (>51)	98
 (1.2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 1 h	 (38)	247
 (1)	Tos-  N=C	NaH, DMSO, Et ₂ O, 15°, 3 h	 (95)	152
 (1)	Tos-  N=C	NaH, DMSO, Et ₂ O, 15°, 3 h	 (100)	152
 (2)	TosCH ₂ N=C	NaOH (40%), TBAI, CH ₂ Cl ₂ , rt, 2 h	 I (79)	73, 98
 (—)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂	 I (85)	161
 (—)	Tos-  N=C	NaOH (30%), TBAI, CH ₂ Cl ₂	 I (82)	161
 (2)	Tos-  N=C	NaH, DMSO, Et ₂ O, rt, 1 h	 I (66)	73
 (2)	TosCH ₂ N=C	NaOH (40%), TBAI, CH ₂ Cl ₂ , rt, 40 min	 I (78)	73
 (2)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O	 I (80)	35
 (1)	Tos-  N=C	<i>t</i> -BuOK, THF, -40° to rt, 2 h	 (70)	93
 (1)	Tos-  N=C	NaH, DMSO, Et ₂ O, 15°, 3 h	 (90)	105

TABLE VIIA. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
 (1)		sl. add. to NaOH (16%), TBAI, CH ₂ Cl ₂ , reflux, 8.5 h	 (>43)	92
(1)		sl. add. to NaOH (16%), TBAI, CH ₂ Cl ₂ , reflux, 9 h	 (>17)	92
(1)		sl. add. to NaOH (16%), TBAI, CH ₂ Cl ₂ , reflux, 13 h	 (>57)	92
 (1)		sl. add. to NaOH (10%), TBAI, CH ₂ Cl ₂ , reflux, 8.5 h	 (>10)	92
(1)		sl. add. to NaOH (13%), TBAI, CH ₂ Cl ₂ , reflux, 8 h	 (>29)	92
 (1)		NaOH, TBAI, CH ₂ Cl ₂	 (>59)	193a
 (—)		NaOH, TBAI, CH ₂ Cl ₂	 (>68) (>57) (>55) (>51)	248

X
F
Cl
Br
I

TABLE VIIA. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

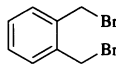
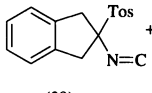
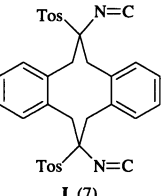
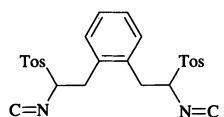
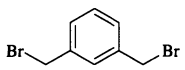
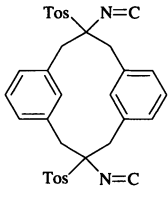
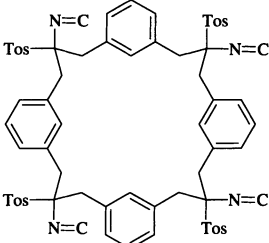
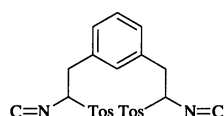
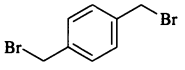
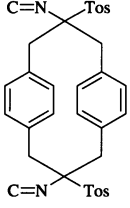
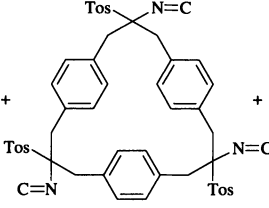
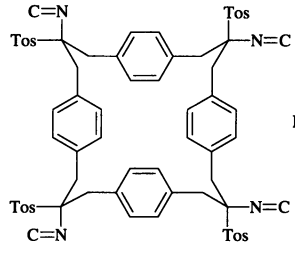
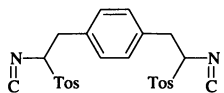
Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
 (1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 24 h	 (39) +  I (7)	153
(1)		NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 24 h	I (47)	153
 (1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 2 h	 I (>48)	155
(1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 24 h	I (14) +  II (-)	153
(1.35)		NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 7.5 h	I (55)	155
(1)	"	NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 2.4 h	I (63) + II (-)	153
 (1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux	 I (>14) +  II (>23) +  III (>12)	155
(1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 24 h	I (0.6) + II (12)	153
(1)		NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 24 h	I (7) + III (-)	153

TABLE VIIA. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.	
(1.35)		NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 7 h	(>52)	155	
(1)		NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 6 h	(>28)	249	
	(2) TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 1.5 h	I (71)	73	
	(2) TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , rt, 6 h	I (78)	161	
	(1.1)	NaH, DMSO, Et ₂ O, 35°, 30 min	(80)	238	
	(1.1)	NaH, DMSO, Et ₂ O	(80)	239	
<i>n</i> -C ₈ H ₁₇ I	(2) TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 3 h	(90)	105	
	(1)	NaH, DMSO, Et ₂ O, rt, 1 h	I (91)	73	
	(1.1) "	NaOH (40%), TBAI, CH ₂ Cl ₂ , rt, 1 h	I (>80)	98	
C ₉		(1) TosCH ₂ N=C	1. NaOH (38%), CH ₂ Cl ₂ , reflux, sl. add., 8 h 2. reflux, 2 h	I (>25)	108
	(1) TosCH ₂ N=C	NaH, DMF, rt, 5 h	I (>7)	154	
	(1.3) TosCH ₂ N=C	NaH, DMF, rt, 5 h	I (>11)	109	
			(>14) R = OMe		

TABLE VIII. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
(1.2)	TosCH ₂ N=C	1. NaOH (30%), CH ₂ Cl ₂ , TBAI, reflux, sl. add., 8.5 h 2. reflux, 15 h	I (>19)	110
		1. NaOH (25%), CH ₂ Cl ₂ , TBAI, reflux, sl. add., 6 h 2. reflux, 5 h	 (>57) R = OMe	110
(1)		NaH, DMSO, Et ₂ O, rt, 1 h	 (90)	105
(1)	TosCH ₂ N=C	KH, THF, rt, 6 h	 (59)	149
THPO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -Br (2)	TosCH ₂ N=C	NaOH (40%), TBAB, CH ₂ Cl ₂ , rt	 (85)	151
C ₁₀ (2S)- (2)	TosCH ₂ N=C	NaOH (40%), TBAB, CH ₂ Cl ₂ , rt	 (82)	151
(1)		NaH, DMSO, Et ₂ O	 (83)	151
(—)	TosCH ₂ N=C	NaOH, TBAB	 (>11)	250
(1)		NaH, DMSO, Et ₂ O, rt, 2 h	 (90)	240, 105
(1)		NaH, DMSO, Et ₂ O, rt, 3 h	 (>67)	237
(1)		NaH, DMSO, Et ₂ O, rt, 3 h	 (—)	237
C ₁₁ MeO ₂ C-CH ₂ -CH ₂ -CH ₂ -Br (1)		NaH, DMSO, Et ₂ O, rt, 18 h	 (50)	160
C ₁₂ (1.35)		NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 7.5 h	 (>44)	155

TABLE VIIA. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

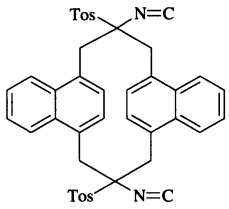
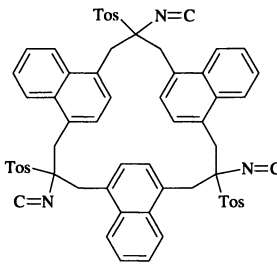
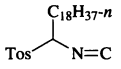
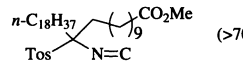
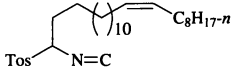
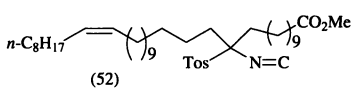
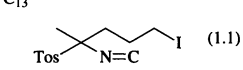
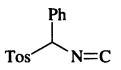
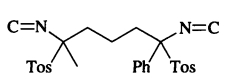
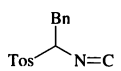
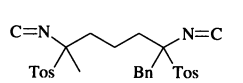
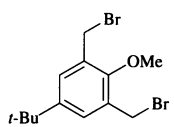
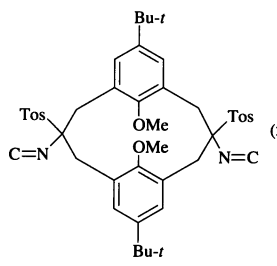
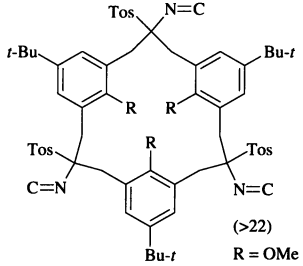
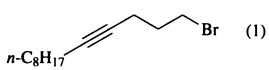
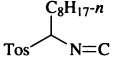
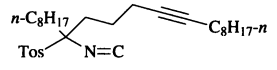
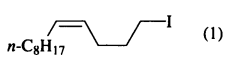
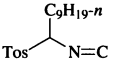
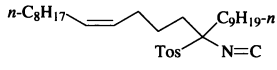
Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
(1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 2 h	 (>14) +	155
(1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 2 h	 (>7)	
MeO ₂ C(CH ₂) ₉ Br (1)		NaH, DMSO, Et ₂ O, 40°, 2 h	 (>70)	242
(1)		NaH, DMSO, Et ₂ O, rt, 18 h	 (52) (>70)	160
C ₁₃  (1.1)		NaH, DMSO, Et ₂ O, reflux, 1 h	 (73)	100
(1.1)		NaH, DMSO, Et ₂ O, reflux, 1 h	 (80)	100
 (—)	TosCH ₂ N=C	1. NaH, DMF, sl. add. 2. rt, 6 h	 (>10) +	156
			 (>22) R = OMe	
 (1)		NaH, DMSO, Et ₂ O, rt, 3 h	 (91)	105
 (1)		NaH, DMSO, Et ₂ O, rt, 3 h	 (85)	105

TABLE VIII. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

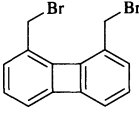
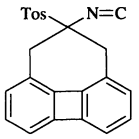
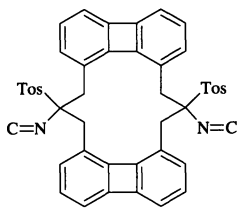
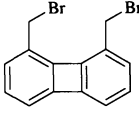
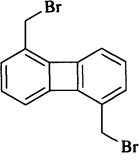
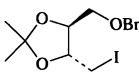
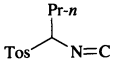
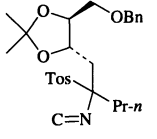
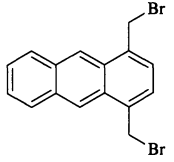
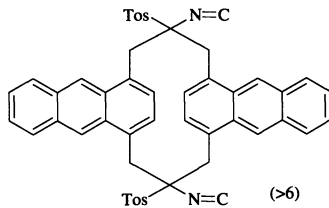
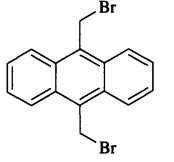
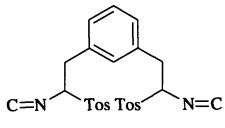
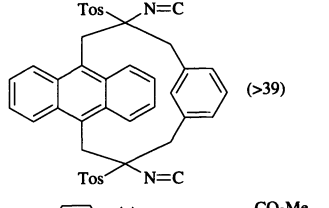
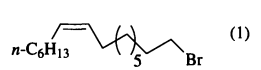
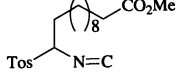
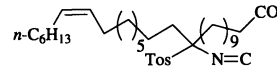
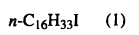
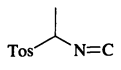
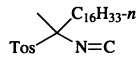
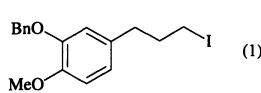
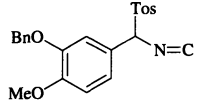
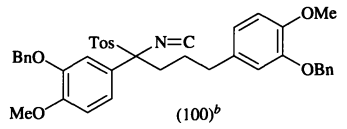
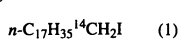
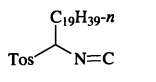
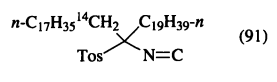
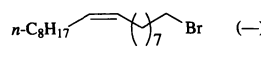
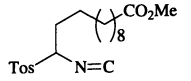
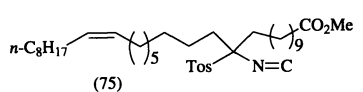
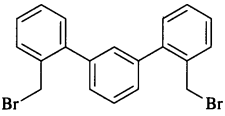
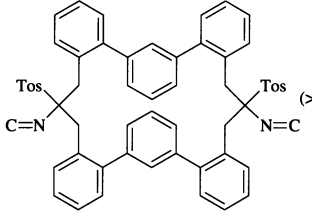
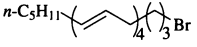
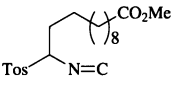
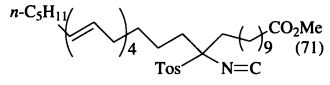
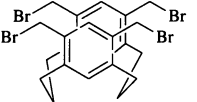
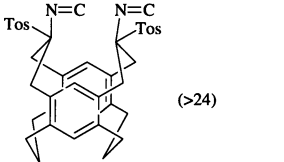
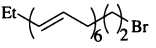
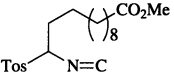
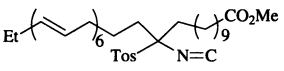
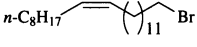
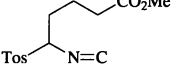
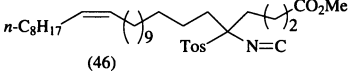

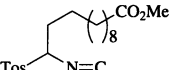
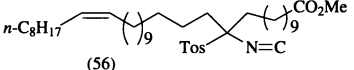
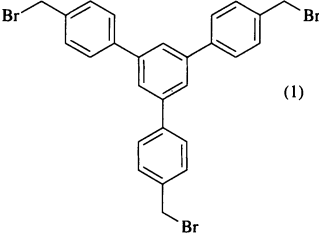
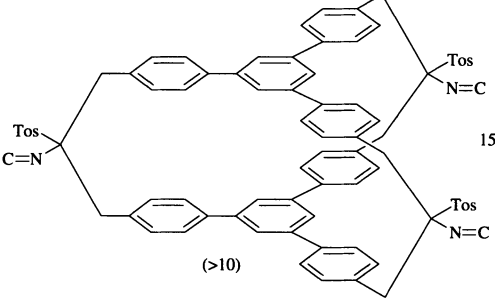
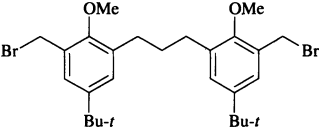
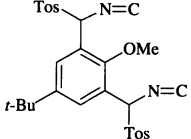
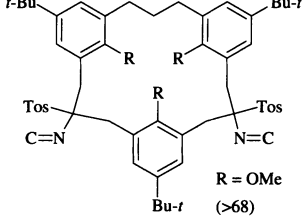
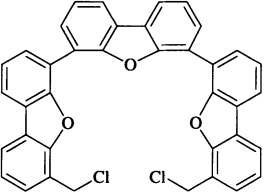
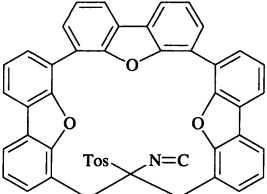
Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O	 I (>17) +  II (>17)	111
 +  1:1	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 12 h	I (>17) + II (>34)	251
		NaH, DMSO, Et ₂ O, 0°, 2 h	 (50)	105
C ₁₆  (1)	TosCH ₂ N=C	NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 2 h	 (>6)	155
 (1.35)		NaOH (30%), TBAI, CH ₂ Cl ₂ , reflux, 7.5 h	 (>39)	155
 (1)		NaH, DMSO, Et ₂ O, rt, 18 h	 (68)	160
 (1)		NaH, DMSO, Et ₂ O, rt, 1 h	 (72)	73
C ₁₇  (1)		<i>t</i> -BuOK, 18-crown-6, THF, -10 to 20°	 (100) ^b	96
C ₁₈  (1)		NaH, DMSO, Et ₂ O, rt, 3 h	 (91)	243
 (—)		NaH, DMSO, Et ₂ O, 35°, 4 h	 (75)	252

TABLE VIIA. DISUBSTITUTED DERIVATIVES OF TOSMIC (Continued)

Substrate (equiv)	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₀  (1)	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 6 h	 (>5)	253
 (1)		NaH, DMSO, Et ₂ O, rt, 18 h	 (71)	160
C ₂₂  (0.5)	TosCH ₂ N=C	NaOH (30%), TBAL, CH ₂ Cl ₂ , rt, 5 h	 (>24)	254
 (1)		NaH, DMSO, Et ₂ O, rt, 18 h	 (60)	160
 (1)		NaH, DMSO, Et ₂ O, rt, 18 h	 (46)	160
 (1)		NaH, DMSO, Et ₂ O, rt, 18 h	 (56)	160
C ₂₇  (1)	TosCH ₂ N=C	NaH, DMF, rt, 5 h	 (>10)	154
 (1)		NaH, DMF, sl. add., 6 h; rt, 5 h	 R = OMe (>68)	156
C ₃₈  (1)	TosCH ₂ N=C	KH, THF, sl. add., 26 h; rt, 2 d	 (>7)	150

^a Halide was added to the mixture of isocyanide and base.

^b The yield is that of the crude product.

TABLE VIII. DISUBSTITUTED DERIVATIVES OF TOSMIC FROM 1-ISOCYANO-1-SULFONYLALKENES

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.													
C ₁		NaOH (50%), BTEAC, CH ₂ Cl ₂ , rt, 2 h	(95)	101													
		NaOH (50%), BTEAC, CH ₂ Cl ₂ , rt, 2 h	$\frac{X}{Cl}$ (89) Br (76)	101													
	MeI		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(69)	103												
			<i>t</i> -BuOK, DME, -30 to 20°, 1 h	$\frac{n}{1}$ (82) 2 (79) 3 (81)	103												
			<i>t</i> -BuOK, DME or THF, -45 to 0°, 2 h	(>55)	235												
			<i>t</i> -BuOK, DME or THF, -45 to 0°, 2 h	(>58) (>51) (>61) (>62) (>81)	235												
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>OH</td> <td>H</td> </tr> <tr> <td>OH</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>OH</td> </tr> <tr> <td>OTMS</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	H	H	OH	H	OH	Me	Me	OH	OTMS	H			
	R ¹	R ²															
	H	H															
	OH	H															
OH	Me																
Me	OH																
OTMS	H																
		<i>t</i> -BuOK, DME or THF, -45 to 0°, 2 h	(97)	101													
		<i>t</i> -BuOK, DME or THF, -45 to 0°, 2 h	(97)	101													
		<i>t</i> -BuOK, DME or THF, -45 to 0°, 2 h	(88)	101													
		NaOH (50%), BTEAC, C ₆ H ₆ , 80°, 1 h	(94)	101													

564

565

TABLE VIII. DISUBSTITUTED DERIVATIVES OF TOSMIC FROM 1-ISOCYANO-1-SULFONYLALKENES (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
		NaOH (50%), BTEAC, C ₆ H ₆ , 80°, 1 h	(95)	101
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(98)	101
C ₂ Br-CH ₂ -CH ₂ -Br		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(69)	103
R-CH ₂ -X		NaOH (50%), BTEAC, C ₆ H ₆ , 80°, 1 h	(89) X R I Me (89) Cl MeO (74)	101
C ₃ CH ₂ =CH-CH ₂ -Br		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(76)	103
Br-CH ₂ -CH ₂ -CH ₂ -Br		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(59)	103
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	$\frac{n}{1}$ (51) $\frac{n}{2}$ (59) $\frac{n}{3}$ (76)	103
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	$\frac{n}{1}$ (29) $\frac{n}{2}$ (32)	103
		DMSO, THF, rt, 1 h; 60°, 3.5 h	(85)	102
C ₄₋₈ R-CH ₂ -Br		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	$\frac{R}{CO_2Et}$ (68) Ph (61) Bz (75)	103
C ₇ 		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(81)	103
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(63)	103
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	(48)	103

TABLE VIII. DISUBSTITUTED DERIVATIVES OF TOSMIC FROM 1-ISOCYANO-1-SULFONYLALKENES (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	 (62)	103
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	 (59)	103
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	 (83)	103
			 (84)	
		NaOH (50%), BTEAC, C ₆ H ₆ , 80°, 1 h	 (50)	101
		NaOH (50%), BTEAC, C ₆ H ₆ , 80°, 1 h	 (54)	101
		NaOH (50%), BTEAC, C ₆ H ₆ , 80°, 1 h	 (80)	101
		<i>t</i> -BuOK, DME, -30 to 20°, 1 h	 (83)	103

TABLE VIIC. α -ISOCYANO- α -TOSYL KETONES FROM TOSMIC HOMOLOGS AND CARBOXYLIC CHLORIDES


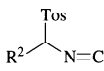
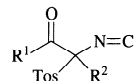
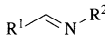
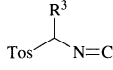
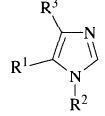
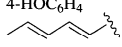
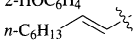
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-7}  R^1 Me <i>t</i> -Bu Ph Ph 4-O ₂ NC ₆ H ₄ 4-O ₂ NC ₆ H ₄	 R^2 Ph Bn Ph Bn Ph Bn	<i>n</i> -BuLi, THF, -80° to rt	 (72) (54) (72) (58) (57) (77)	112

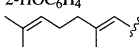
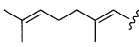
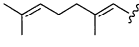
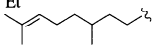
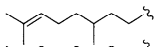
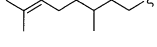
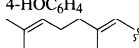
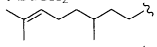
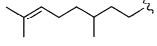
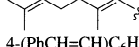
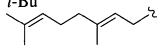
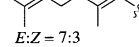
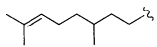
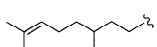
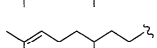
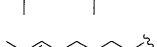
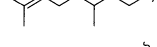
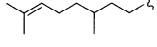
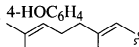
TABLE VIII. IMIDAZOLES FROM ALDIMINES

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-23} 				
R^1	R^2			
R^3				
C_4 Me	Et	H	<i>t</i> -BuNH ₂ , DME, rt, 20 h	(70) 37
Me	Et	H	K ₂ CO ₃ , MeOH, rt, 20 h	(62) 37
C_6 Me	<i>t</i> -Bu	H	<i>t</i> -BuNH ₂ , MeOH, rt, 20 h	(94) 37
Me	<i>t</i> -Bu	H	<i>t</i> -BuNH ₂ , DME, rt, 20 h	(90) 37
Me	<i>t</i> -Bu	H	K ₂ CO ₃ , MeOH, rt, 20 h	(54) 37
Me	<i>t</i> -Bu	Ph	<i>t</i> -BuNH ₂ , DME, rt, 0.5 h	(89) 37
<i>t</i> -Bu	Me	H	<i>t</i> -BuNH ₂ , MeOH, rt, 72 h	(96) 37
<i>t</i> -Bu	Me	H	K ₂ CO ₃ , MeOH, rt, 20 h	(5) 37
C_7 <i>i</i> -Pr	<i>i</i> -Pr	H	<i>i</i> -PrNH ₂ , MeOH, rt, 16 h	(75) 37
C_8 4-O ₂ NC ₆ H ₄	Me	H	K ₂ CO ₃ , MeOH, rt, 16 h	(14) 37
4-O ₂ NC ₆ H ₄	Me	H	<i>i</i> -PrNH ₂ , MeOH, rt, 100 h	(0) 37
Ph	Me	H	K ₂ CO ₃ , MeOH, DME, 0°, 60 h	(10) 37
Ph	Me	Ph	K ₂ CO ₃ , MeOH, rt, 16 h	(90) 37
Me	C ₆ H ₁₁	H	C ₆ H ₁₁ NH ₂ , MeOH, rt, 17 h	(96) 37
Me ₂ C=CH	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(40) 115
C_9 4-MeC ₆ H ₄	Me	H	K ₂ CO ₃ , MeOH, rt, 20 h	(37) 37
2-HOC ₆ H ₄	Et	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(50) 255
4-HOC ₆ H ₄	Et	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(30) 256
	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(14) 115
Me ₂ C=CH	<i>i</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(67) 114
C_{10} 2-ClC ₆ H ₄	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(0.8) 115
3-ClC ₆ H ₄	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(2.5) 115
4-FC ₆ H ₄	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(1) 115
3-HOC ₆ H ₄	<i>i</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(59) 232
Bn	Et	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(9) 255
C_{11} 4-CF ₃ C ₆ H ₄	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(0.3) 115
3-HOC ₆ H ₄	<i>i</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(43) 257
3-HOC ₆ H ₄	<i>i</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(24) 114
2-HOC ₆ H ₄	<i>i</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(78) 121
2-HOC ₆ H ₄	<i>n</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(78) 121
4-HOC ₆ H ₄	<i>n</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(75) 256
4-MeC ₆ H ₄	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(7) 115
C_{12} Me ₂ C=CH	Bn	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(20) 114
3,4-Cl ₂ C ₆ H ₃	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(1) 258
4-BrC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(1) 258
4-O ₂ NC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(1) 258
2-HOC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(82) 121
3-HOC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(33) 258
2-HOC ₆ H ₄	<i>n</i> -C ₅ H ₁₁	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(73) 121
<i>n</i> -C ₆ H ₁₃ 	<i>n</i> -Pr	II	K ₂ CO ₃ , MeOH, reflux, 3 h	(33) 115
C_{13} 4-ClC ₆ H ₄	4-ClC ₆ H ₄	H	K ₂ CO ₃ , MeOH, DME, rt, 16 h	(43) 37
4-ClC ₆ H ₄	4-ClC ₆ H ₄	H	1. NaH, DME, -20°, 3 h ^d	(40) 37
4-O ₂ NC ₆ H ₄	4-O ₂ NC ₆ H ₄	H	K ₂ CO ₃ , MeOH, DME, rt, 16 h	(87) 37
4-O ₂ NC ₆ H ₄	4-O ₂ NC ₆ H ₄	H	<i>t</i> -BuNH ₂ , DME, rt, 24 h	(0) 37
Ph	4-O ₂ NC ₆ H ₄	H	K ₂ CO ₃ , MeOH, DME, reflux, 1 h	(70) 37
Ph	4-O ₂ NC ₆ H ₄	H	K ₂ CO ₃ , MeOH, DME, 20°, 3 h	(34) 37
Ph	4-O ₂ NC ₆ H ₄	H	1. NaH, DME, -20°, 1 h ^d	(65) 37
			2. K ₂ CO ₃ , MeOH, reflux, 0.5 h	
Ph	4-O ₂ NC ₆ H ₄	Me	NaH, DME, 0°, 1 h	(75) 37, 69
4-O ₂ NC ₆ H ₄	Ph	H	K ₂ CO ₃ , MeOH, DME, rt, 16 h	(82) 37
4-O ₂ NC ₆ H ₄	Ph	Me	<i>t</i> -BuOK, DMSO	(78) 69
4-O ₂ NC ₆ H ₄	Ph	Bn	<i>t</i> -BuOK, DMSO	(62) 69
4-ClC ₆ H ₄	Ph	Bn	NaH, DMSO	(68) 69
Ph	Ph	Ph	<i>t</i> -BuNH ₂ , DME, rt, 16 h	(0) 37

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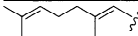
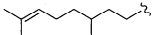
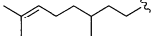
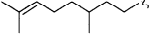
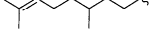
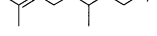

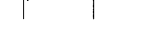


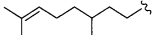
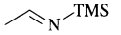
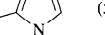
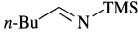
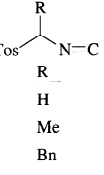
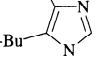
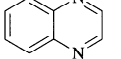
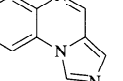
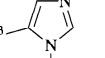
TABLE VIII. IMIDAZOLES FROM ALDIMINES (Continued)

Substrate		Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
R ¹	R ²	R ³			
Ph	Ph	Ph	NaH, DME, 25°, 1 h	(0)	37
Ph	Ph	H	1. NaH, DME, -20°, 3 h ^a 2. K ₂ CO ₃ , MeOH, reflux, 0.5 h	(56)	37
Ph	Ph	H	K ₂ CO ₃ , MeOH, reflux, 2.5 h	(10)	256
Ph	Ph	H	1. K ₂ CO ₃ , MeOH, rt, 70 h 2. reflux, 0.5 h	(0)	37
3,4-(OCH ₂ O)C ₆ H ₃	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(4)	258
2-MeC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(6)	258
3-MeC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(4)	258
4-MeC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(4)	258
4-MeOC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(41)	258
4-HOC ₆ H ₄	<i>n</i> -C ₆ H ₁₃	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(77)	256
2-HOC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(61)	121
	<i>n</i> -Pr	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(25)	115
C ₁₄ Ph	Bn	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(4)	259
2-HOC ₆ H ₄	Bn	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(56)	121
4-MeC ₆ H ₄	Ph	H	1. NaH, DME, -20°, 3 h ^a 2. K ₂ CO ₃ , MeOH, reflux, 0.5 h	(19)	37
4-HOC ₆ H ₄	C ₆ H ₁₁ CH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(50)	256
4-EtC ₆ H ₄	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(7)	258
	<i>s</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(—)	257
	<i>i</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(23)	114
C ₁₅ 2-HOC ₆ H ₄	BnCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(72)	121
4-PhOC ₆ H ₄	Et	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(47)	255
2-C ₄ H ₃ O		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(5)	260
2-C ₄ H ₃ S		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(2)	260
3-C ₄ H ₃ S		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(11)	260
4-HOC ₆ H ₄	<i>n</i> -C ₈ H ₁₇	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(77)	256
	<i>n</i> -C ₃ H ₁₁	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(—)	257
C ₁₆ 1-C ₁₀ H ₇	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(3)	258
2-C ₁₀ H ₇	<i>t</i> -BuCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(2)	258
2-C ₃ H ₄ N		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(2)	260
4-C ₃ H ₄ N		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(3)	260
	C ₆ H ₁₁	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(—)	257
C ₁₇ 4-(PhCH=CH)C ₆ H ₄	Et	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(39)	255
4-PhOC ₆ H ₄	<i>i</i> -Bu	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(7)	257
4-HOC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(89)	256
	Bn	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(<i>E</i>)- (25), (<i>Z</i>)- (10)	259
<i>E:Z</i> = 7:3	4-ClC ₆ H ₄ CH ₂	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(<i>E</i>)- (13)	259
<i>E:Z</i> = 7:3		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(2)	260
2,4-Cl ₂ C ₆ H ₃		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(2)	260
2-ClC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(2)	260
3-ClC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(3)	260
4-O ₂ NC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(4)	260
Ph		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(12)	260
4-HOC ₆ H ₄	<i>n</i> -C ₁₀ H ₂₁	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(72)	256
C ₁₈ 4-HOC ₆ H ₄	1-C ₁₀ H ₇ CH ₂	H	K ₂ CO ₃ , MeOH, reflux, 2 h	(2)	256
	BnCH ₂	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(<i>E</i>)- (23)	259
<i>E:Z</i> = 7:3					

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TABLE VIII. IMIDAZOLES FROM ALDIMINES (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.	
R^1  $E:Z = 7:3$	R^2 2-MeC ₆ H ₄ CH ₂	R^3 H	K ₂ CO ₃ , MeOH, reflux, 3 h	(E)- (31)	259
$E:Z = 7:3$	4-MeC ₆ H ₄ CH ₂	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(E)- (24)	259
$E:Z = 7:3$	4-MeOC ₆ H ₄ CH ₂	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(E)- (31)	259
$E:Z = 7:3$	(S)-PhCH(Me)	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(E)-(S)- (19)	259
$E:Z = 7:3$	(R)-PhCH(Me)	H	K ₂ CO ₃ , MeOH, reflux, 3 h	(E)-(R)- (17)	259
$E:Z = 7:3$ 2-MeC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(7)	260
2-MeOC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(31)	260
4-MeOC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(22)	260
3,4-(OCH ₂) ₂ C ₆ H ₃		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(13)	260
C ₁₉ 2-EtOC ₆ H ₄		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(27)	260
3,4-(MeO) ₂ C ₆ H ₃		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(14)	260
2,4-(MeO) ₂ C ₆ H ₃		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(36)	260
C ₂₀ $E:Z = 7:3$		H	K ₂ CO ₃ , MeOH, reflux, 3 h	(E)- (12)	259
C ₂₁ 1-C ₁₀ H ₇		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(4)	260
2-C ₁₀ H ₇		H	K ₂ CO ₃ , MeOH, reflux, 2 h	(6)	260
BnO(CH ₂) ₃	BnO(CH ₂) ₃	H	—	(—)	261
C ₂₃ BnO(CH ₂) ₄	BnO(CH ₂) ₄	H	—	(—)	261
C ₅ 	TosCH ₂ N=C		LiN(TMS) ₂ , THF, -78°, 2 h; rt, 16 h	 (55)	113
C ₈ 			LiN(TMS) ₂ , THF, -78°, 2 h; rt, 16 h	 (51) (51) (66)	113
	TosCH ₂ N=C		<i>n</i> -BuLi (2 eq), [CuI*(<i>n</i> -Bu) ₃ P], -70 to 0°, 4 h	 (30)	79
C ₈₋₁₄ R^1 -CH=CH-N ⁻ -R ²	TosCH ₂ N=C		1. K ₂ CO ₃ , MeOH, reflux, 3 h 2. NaH, DMF, rt, 1 h 3. BnCl, rt, 10 h		232
	R^1	R^2		R^3	
C ₈	3-HOC ₆ H ₄	Me		3-BnOC ₆ H ₄	(36)
C ₉	3-HOC ₆ H ₄	Et		3-BnOC ₆ H ₄	(13)
C ₁₀	2-HOC ₆ H ₄	<i>i</i> -Pr		2-BnOC ₆ H ₄	(66)
	4-HOC ₆ H ₄	<i>i</i> -Pr		4-BnOC ₆ H ₄	(19)
	3-HOC ₆ H ₄	<i>n</i> -Pr		3-BnOC ₆ H ₄	(8)
C ₁₁	3-HOC ₆ H ₄	<i>n</i> -Bu		3-BnOC ₆ H ₄	(10)
	3-HOC ₆ H ₄	<i>i</i> -Bu		3-BnOC ₆ H ₄	(5)
C ₁₂	3-HOC ₆ H ₄	<i>t</i> -BuCH ₂		3-BnOC ₆ H ₄	(33)
C ₁₄	3-HOC ₆ H ₄	Bn		3-BnOC ₆ H ₄	(15)

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TABLE VIII. IMIDAZOLES FROM ALDIMINES (Continued)

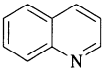
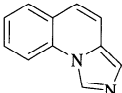
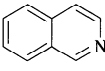
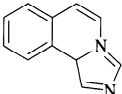
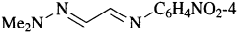
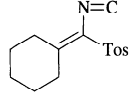
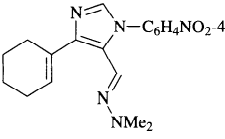
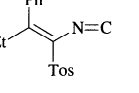
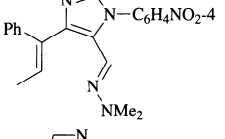
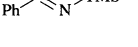
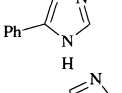
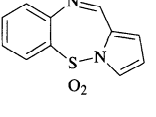
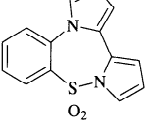
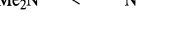
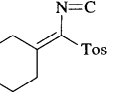
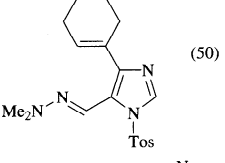
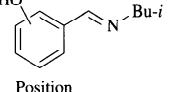
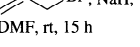
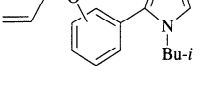
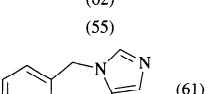
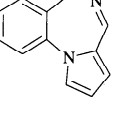
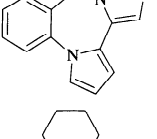
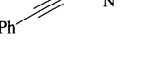
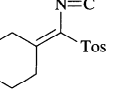
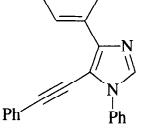
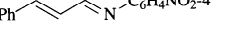
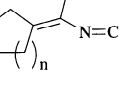
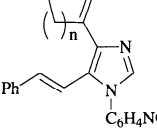
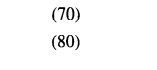
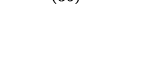
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), LiBr, THF, -70 to 0°, 4 h	 (25)	79
	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), LiBr, THF, -70 to 0°, 4 h	 (44)	79
C ₁₀ 		Triton B, THF, 20-30°, 1.5 h	 (85)	63
		Triton B, THF, 20-30°, 1.5 h	 (99)	63
	TosCH ₂ N=C	LiN(TMS) ₂ , THF, -78°, 2 h; rt, 16 h	 (23)	113
C ₁₁ 	TosCH ₂ N=C	<i>n</i> -BuLi, THF, -72°, 30 min; rt, 60 h	 (39)	262
		<i>t</i> -BuOK, THF, -80°; rt, 5 h	 (50)	63
	TosCH ₂ N=C	1. K ₂ CO ₃ , MeOH, reflux, 3 h 2.  , NaH, DMF, rt, 15 h	 (62)  (55)	114
C ₁₂ 	TosCH ₂ N=C	<i>n</i> -BuLi (2 eq), THF, -50°, 30 min; rt, 36 h	 (61)	8, 263
C ₁₅ 		<i>t</i> -BuOK, THF, -78 to 20°, 2 h	 (29)	80
		<i>t</i> -BuOK, THF, -78 to 20°, 2 h	 (70)  (70)  (80)	80
	$\frac{n}{1}$ 2 3			

TABLE VIII. IMIDAZOLES FROM ALDIMINES (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆				
	TosCH ₂ N=C	<i>t</i> -BuOK, MeOH, reflux, 4 h	(75)	34
		<i>t</i> -BuOK, THF, -78 to 20°, 2 h	(34)	80
C ₂₀				
		NaH, DMSO, 80°, 4 h	(16) +	264
			(6)	
		NaH, DMSO, 80°, 4 h	(31)	264
		NaH, DMSO, 80°, 4 h	(8)	116
$\frac{X}{Cl}$ Br			(5)	
		NaH, DMSO, 80°, 4 h	(56)	116
$\frac{X}{Cl}$ Br			(45)	
C ₃₁				
	TosCH ₂ N=C	BnNH ₂ , MeOH, rt, overnight	(>97)	265

^a The intermediate 4-tosyl-2-imidazole was isolated and used as such in a second reaction.

578

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TABLE VIII B. 4-TOSYLIMIDAZOLES FROM IMIDOYL CHLORIDES OR ISOTHIOCYANATES

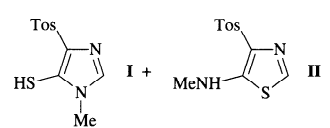
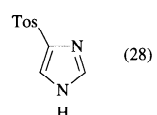

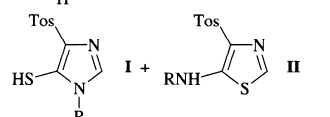
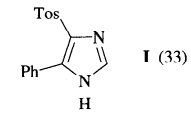
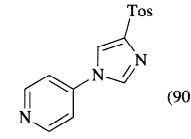
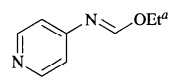
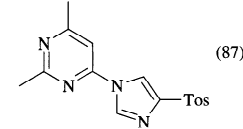
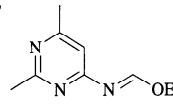
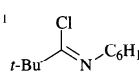
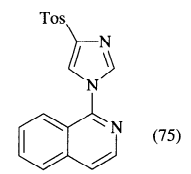
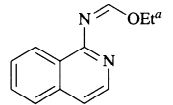
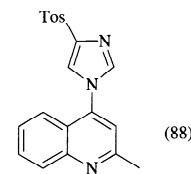
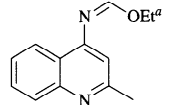
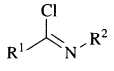
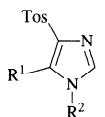
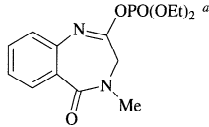
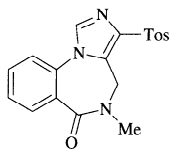
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
$\text{Me}-\text{N}=\text{C}=\text{S}$	TosCH ₂ N=C	<i>t</i> -BuLi (2 eq), THF, -70 to -10°, 10 min	I (54)	120
	TosCH ₂ N=C	NaH, DME, rt, 0.5 h	II (72)	120
C ₃				
	TosCH ₂ N=C	EtONa, EtOH, DMF, sl. add., rt, 8 h; rt, 16 h	(28)	118
C ₃₋₉				
$\text{R}-\text{N}=\text{C}=\text{S}$	TosCH ₂ N=C		I + II	120
<u>R</u>				
Et		<i>t</i> -BuLi (2 eq), THF, -70 to -10°, 10 min	I (20) + II (50)	
4-O ₂ NC ₆ H ₄		NaOH (4%), TBAB, C ₆ H ₆ , rt, 1 h	I (65) + II (10)	
Ph		NaH, DMSO, rt, 1 h	I (83)	
Ph		NaOH (4%), TBAB, CH ₂ Cl ₂ , rt, 1 h	II (67)	
4-Me ₂ NC ₆ H ₄		NaH, DMSO, rt, 1 h	I (79) + II (9)	
C ₆ H ₁₁		<i>t</i> -BuLi (2 eq), THF, -70 to -10°, 10 min	I (40) + II (35)	
PhCN ^a	TosCH ₂ N=C	<i>t</i> -BuLi (2 eq), THF, -70 to 0°, 20 min		79
	TosCH ₂ N=C	<i>t</i> -BuOK, HMPA, rt, 6 d	I (48)	79
C ₈				
	TosCH ₂ N=C	NaH, DME, rt, 2 h	(90)	119
C ₉				
	TosCH ₂ N=C	NaH, DME, -30°, 2 h	(87)	119
C ₁₁				
	TosCH ₂ N=C	NaH, DMSO + DMF, or DME, rt	(0)	37, 266
C ₁₂				
	TosCH ₂ N=C	NaH, DMSO + DMF, or DME, rt	(75)	119
C ₁₃				
	TosCH ₂ N=C	NaH, DME, rt, 2 h	(88)	119

TABLE VIII.B. 4-TOSYLIMIDAZOLES FROM IMIDOYL CHLORIDES OR ISOTHIOCYANATES (*Continued*)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.												
	TosCH ₂ N=C	NaH, DME, rt, 2 h		37, 266												
<table border="0"> <tr> <td>R¹</td> <td>R²</td> </tr> <tr> <td>Ph</td> <td>4-O₂NC₆H₄</td> </tr> <tr> <td>4-O₂NC₆H₄</td> <td>Ph</td> </tr> <tr> <td>Ph</td> <td>Ph</td> </tr> <tr> <td>4-O₂NC₆H₄</td> <td>C₆H₁₁</td> </tr> <tr> <td>Ph</td> <td>C₆H₁₁</td> </tr> </table>	R ¹	R ²	Ph	4-O ₂ NC ₆ H ₄	4-O ₂ NC ₆ H ₄	Ph	Ph	Ph	4-O ₂ NC ₆ H ₄	C ₆ H ₁₁	Ph	C ₆ H ₁₁		NaH, DME, DMSO, rt, 1 h	(81)	
R ¹	R ²															
Ph	4-O ₂ NC ₆ H ₄															
4-O ₂ NC ₆ H ₄	Ph															
Ph	Ph															
4-O ₂ NC ₆ H ₄	C ₆ H ₁₁															
Ph	C ₆ H ₁₁															
		NaH, DME, DMSO, rt, 1 h	(85)													
		NaH, DME, DMSO, rt, 1 h	(60)													
		NaH, DME, THF, rt, 1 h	(75)													
		NaH, DME, THF, rt, 1 h	(80)													
C ₁₄ 	TosCH ₂ N=C	LDA, THF, -78°, 2 h 40, 281	 (46)	117												

^a This reaction involves a leaving group other than the Cl of an imidoyl chloride.

TABLE VIII. IMIDAZOLES FROM 1-ISOCYANO-1-TOSYLALKENES

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ MeNH ₂		MeOH	(55)	234
C ₀₋₈ R ¹ NH ₂				126
R ¹	R ² = 4-MeC ₆ H ₄ CO ₂ -	MeOH, rt, 5 h	(86)	
H		MeOH, rt, 30 min	(56)	
Bn		1. POCl ₃ , TEA, -5°, 1 h ^b	(44)	
4-O ₂ NC ₆ H ₄ (CH ₂) ₂ ^a		2. substrate, NaOMe, -5°, 30 min		
R ¹ NH ₂		MeOH, rt		
R ¹	R ²			
C ₀ H	Ph	3 h	(65)	86
C ₁ Me	H	15 min	(5)	86
Me	<i>t</i> -Bu	10 min	(46)	86
Me	Ph	5 min	(87)	86
Me	4-O ₂ NC ₆ H ₄	3 min	(88)	86
C ₂ Et	Ph	12 h	(38) ^f	256
Et	4-PhC ₆ H ₄	2 d	(18) ^f	255
C ₃ CH ₂ CO ₂ Me	Ph	TEA, 7 d	(53)	121
<i>i</i> -Pr	3-PhOC ₆ H ₄	24 h	(31) ^f	232

TABLE VIII.C. IMIDAZOLES FROM 1-ISOCYANO-1-TOSYLALKENES (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
R^1NH_2		MeOH, rt		
R^1	R^2			
<i>n</i> -Pr	4-BrC ₆ H ₄	24 h	(18)	115
<i>n</i> -Pr	4-ClC ₆ H ₄	24 h	(52)	115
<i>n</i> -Pr	Ph	12 h	(53) ^c	256, 267
C ₄ <i>i</i> -Bu	4-BrC ₆ H ₄	24 h	(47) ^c	114
<i>i</i> -Bu	Ph	3 h	(93)	121
<i>i</i> -Bu	4-PhC ₆ H ₄	24 h	(39) ^c	114
<i>i</i> -Bu	3-PhOC ₆ H ₄	24 h	(23) ^c	232
<i>t</i> -Bu	Ph	24 h	(82)	86
<i>n</i> -Bu	Ph	3 h	(86)	121
<i>n</i> -Bu	3-ClC ₆ H ₄	3 h	(29)	121
C ₅ <i>t</i> -BuCH ₂	Ph	3 h	(79)	121
<i>t</i> -BuCH ₂	4-BrC ₆ H ₄	24 h	(41) ^c	114
<i>t</i> -BuCH ₂	2-ClC ₆ H ₄	3 h	(59)	121
<i>t</i> -BuCH ₂	3-ClC ₆ H ₄	3 h	(25)	121
<i>t</i> -BuCH ₂	4-ClC ₆ H ₄	3 h	(60)	121
<i>n</i> -C ₅ H ₁₁	3-ClC ₆ H ₄	3 h	(25)	121
C ₆ Ph	Ph	—	(0)	86
C ₆ H ₁₁	Ph	30 min	(97)	86
C ₆ H ₁₁	Ph	24 h	(53) ^c	256
<i>t</i> -Bu(CH ₂) ₂	Ph	3 h	(86)	121
C ₇ Bn	Ph	24 h	(—)	267
Bn	PhCH=CH	3 d	(73)	34
C ₈ BnCH ₂	Ph	3 h	(78)	121
C ₉ (CH ₂) ₆ CO ₂ Et	<i>n</i> -C ₅ H ₁₁ CH(OTBDMS)(CH ₂) ₂	Et ₃ N, 17 h	(35) ^d	233
C ₁₀	Ph	24 h	(—)	267
C ₁₁ 1-C ₁₀ H ₁₇ CH ₂	Ph	24 h	(32) ^c	256
C ₁₂ <i>n</i> -C ₁₂ H ₂₅	Ph	24 h	(—)	267

^a The substrate was the amine hydrochloride.

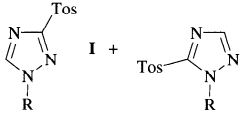
^b A substituted formamide was used instead of an isocyanide; this first step was required to convert it into the isocyanide.

^c The yield was based on the formamide.

^d The yield was based on TosMIC.

TABLE IX. 1,2,4-TRIAZOLES FROM DIAZONIUM SALTS

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Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅₋₁₀ $\overset{+}{\text{R}}\text{N}=\overset{-}{\text{N}}\text{X}$	TosCH ₂ N=C	K ₂ CO ₃ , DMSO, MeOH, H ₂ O, ~-10°	 I + II	122
<u>R</u>	<u>X</u>			
3-C ₅ H ₄ N	Cl	30 min	I (15) + II (3)	
4-O ₂ NC ₆ H ₄	BF ₄	1 h	I (0) + II (0) ^a	
Ph	BF ₄	1 h	I (40) + II (18)	
4-MeOC ₆ H ₄	Cl	30 min	I (80) + II (12)	
4-Me ₂ NC ₆ H ₄	BF ₄	1 h	I (94)	
1-C ₁₀ H ₇	BF ₄	1 h	I (38) + II (3)	

^a *N*-Tosylmethyl-4-nitrobenzamide was obtained in 39% yield.

TABLE X. THIAZOLES FROM THIOCARBONYL COMPOUNDS

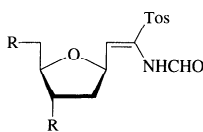
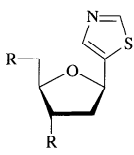
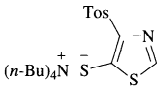
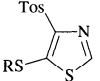
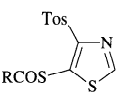
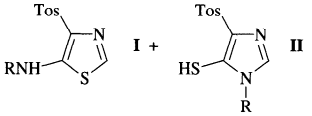
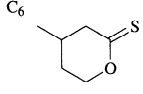
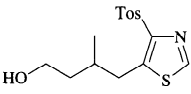
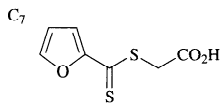
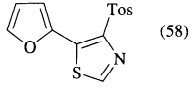
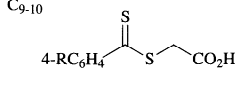
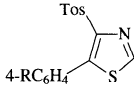
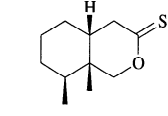
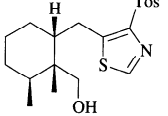
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₀ H ₂ S ^a	 R = 4-MeC ₆ H ₄ CO ₂ ⁻	1. POCl ₃ , TEA, DME, -5°, 1 h 2. Excess substrate, 2 min	 (60)	126												
C ₁ CS ₂	TosCH ₂ N=C	NaOH (10%), CHCl ₃ , TBAB, rt, 1.5 h	 (94)	125												
	TosCH ₂ N=C	1. NaOH (10%), CHCl ₃ , TBAB, rt, 1.5 h 2. RX, CHCl ₃ , rt, 3 h		125												
		<table border="1"> <thead> <tr> <th>R</th> <th>X</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>I</td> </tr> <tr> <td>Et</td> <td>Br</td> </tr> <tr> <td>CH₂=CHCH₂</td> <td>Br</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>Br</td> </tr> <tr> <td>Bn</td> <td>Br</td> </tr> </tbody> </table>	R	X	Me	I	Et	Br	CH ₂ =CHCH ₂	Br	<i>n</i> -Bu	Br	Bn	Br	(90) (93) (94) (91) (94)	
R	X															
Me	I															
Et	Br															
CH ₂ =CHCH ₂	Br															
<i>n</i> -Bu	Br															
Bn	Br															
	TosCH ₂ N=C	1. NaOH (10%), CHCl ₃ , TBAB, rt, 1.5 h 2. RCOCl, CHCl ₃ , 0°, 1 h		125												
		<table border="1"> <thead> <tr> <th>R</th> </tr> </thead> <tbody> <tr> <td>Me</td> </tr> <tr> <td>Ph</td> </tr> </tbody> </table>	R	Me	Ph	(86) (91)										
R																
Me																
Ph																

TABLE X. THIAZOLES FROM THIOCARBONYL COMPOUNDS (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₋₂₀ RN=C=S	TosCH ₂ N=C		 I + II	120
R				
Me		NaH, DME, rt, 0.5 h	I (72)	
Me		<i>n</i> -BuLi (2 eq), THF, -70 to -10°, 10 min	II (54)	
Et		NaH, DMSO, rt, 1 h	I (93)	
Et		<i>n</i> -BuLi (2 eq), THF, -70 to -10°, 10 min	I (50) + II (20)	
CH ₂ =CHCH ₂		NaH, DME, rt, 0.5 h	I (62)	
EtO ₂ C		<i>n</i> -BuLi, THF, -65°, 0.5 h; 0°, 2 h	I (62)	
<i>n</i> -Bu		NaH, DME, rt, 0.5 h	I (77)	
Ph		NaOH (4%), TBAB, CH ₂ Cl ₂ , rt, 1 h	I (67)	
4-O ₂ NC ₆ H ₄		<i>n</i> -BuLi, THF, -65°, 0.5 h; 0°, 2 h	I (56) + II (16)	
C ₆ H ₁₁		NaH, DME, rt, 0.5 h	I (76)	
Bn		NaH, DME, rt, 0.5 h	I (74)	
4-Me ₂ NC ₆ H ₄		NaH, DME, -50°, 0.5 h	I (68) + II (2)	
1-C ₁₀ H ₇		<i>n</i> -BuLi, THF, -65°, 0.5 h; 0°, 2 h	I (38)	
Ph ₃ C		NaH, DME, rt, 0.5 h	I (39)	
	TosCH ₂ N=C	<i>n</i> -BuLi, THF, -78°, 1 h	 (67)	123
C ₇ 	TosCH ₂ N=C (2 eq)	KOH (3 eq), <i>t</i> -BuOH, rt, 6-12 h	 (58)	124
C ₉₋₁₀ 4-RC ₆ H ₄ 	TosCH ₂ N=C (2 eq)	KOH (3 eq), <i>t</i> -BuOH, rt, 6-12 h	 (48)	124
R				
Cl			(53)	
H			(62)	
Me			(79)	
MeO				
C ₁₁ 	TosCH ₂ N=C	<i>n</i> -BuLi, THF, -20°, 2.5 h	 (79)	268, 123

^a The thiazole was formed via an α,β -unsaturated isocyanide and hydrogen sulfide.

TABLE XI-A1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TOSCHRN=C AND MICHAEL ACCEPTORS


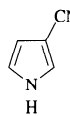
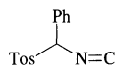
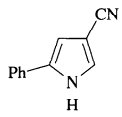
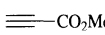
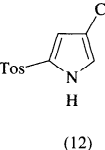
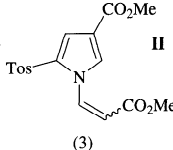
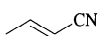
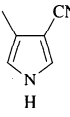
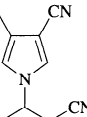
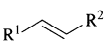
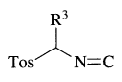
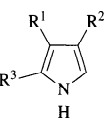
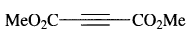
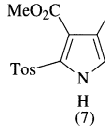
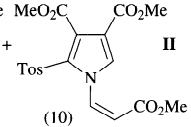
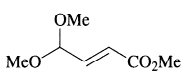
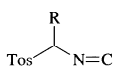
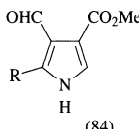
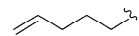
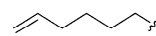
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.																											
C ₃ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-35°, 15 min	 (10)	127																											
		NaH, DMSO, Et ₂ O, rt, 20 min	 (60)	268a																											
C ₄ 	TosCH ₂ N=C	DBU, DMF, -10°, 1 h	 I +  II	140																											
	TosCH ₂ N=C (0.5 eq)	DBU, DMF, rt, 3 h	II (30)	140																											
	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-35°, 15 min	 (50) +  (9)	127																											
																															
	<table border="1" data-bbox="321 975 651 1113"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>CN</td> <td>CN</td> <td>H</td> </tr> <tr> <td>H</td> <td>COMe</td> <td>H</td> </tr> <tr> <td>H</td> <td>COMe</td> <td>Ph</td> </tr> <tr> <td>H</td> <td>CO₂Me</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	CN	CN	H	H	COMe	H	H	COMe	Ph	H	CO ₂ Me	H	NaH, DMF, 0-5°	(79)	130												
R ¹	R ²	R ³																													
CN	CN	H																													
H	COMe	H																													
H	COMe	Ph																													
H	CO ₂ Me	H																													
		NaH, DMF, 0-5°, 15 min	(15)	127																											
		NaH, DMF, 0-5°, 40 min	(64)	268a																											
		NaH, DMF, 0-5°, 15 min	(33)	127																											
C ₅	<table border="1" data-bbox="321 1182 651 1435"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>CF₃</td> <td>COMe</td> <td>H</td> </tr> <tr> <td>-(CH₂)₂CO-</td> <td></td> <td>H</td> </tr> <tr> <td>H</td> <td>CO₂Et</td> <td>Ph</td> </tr> <tr> <td>Me</td> <td>COMe</td> <td>H</td> </tr> <tr> <td>Me</td> <td>COMe</td> <td>H</td> </tr> <tr> <td>Me</td> <td>CO₂Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>CO₂Me</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>CO₂Me</td> <td>Bn</td> </tr> </tbody> </table>	R ¹	R ²	R ³	CF ₃	COMe	H	-(CH ₂) ₂ CO-		H	H	CO ₂ Et	Ph	Me	COMe	H	Me	COMe	H	Me	CO ₂ Me	H	Me	CO ₂ Me	Me	Me	CO ₂ Me	Bn	NaH, DMSO, Et ₂ O, rt, 30 min	(44)	269
R ¹	R ²	R ³																													
CF ₃	COMe	H																													
-(CH ₂) ₂ CO-		H																													
H	CO ₂ Et	Ph																													
Me	COMe	H																													
Me	COMe	H																													
Me	CO ₂ Me	H																													
Me	CO ₂ Me	Me																													
Me	CO ₂ Me	Bn																													
		NaH, DME, -20° to rt, 1 h	(30-50)	270																											
		NaH, DMSO, Et ₂ O, rt, 30 min	(80)	268a																											
		NaH, DMSO, Et ₂ O, 20-35°, 15 min	(45)	127																											
		NaH, DMSO, Et ₂ O, 20-35°, 15 min	(84)	271																											
		NaH, DMSO, Et ₂ O, 20-35°, 15 min	(64)	127																											
		NaH, DMSO, Et ₂ O, rt	(71)	69																											
		NaH, DMSO, Et ₂ O, rt	(81)	69																											
C ₆	2-C ₄ H ₃ S	NO ₂	H	NaH, DMSO, Et ₂ O, 0-5°, 2 h	(43)	272																									
	CN	CO ₂ Et	H	NaH, DMSO, Et ₂ O, rt, 3 h	(54)	134																									
	CO ₂ Me	CO ₂ Me	H	NaH, DMSO, Et ₂ O, 20-35°	(60)	127																									
	CO ₂ Me	CO ₂ Me	CH ₂ TMS	<i>t</i> -BuOK, THF, rt, 17 h	(74)	93																									
	-(CH ₂) ₃ CO-		H	NaH, DME, -20° to rt, 1 h	(30-50)	270																									
	Me	CO ₂ Et	H	NaH, DMSO, Et ₂ O, rt, 15 min	(70)	271, 273																									
	Et	COMe	H	NaH, DMSO, Et ₂ O, rt, 15 min	(91)	271																									
		TosCH ₂ N=C		DBU, DMF, -10°, 1 h	 I +  II	140																									
		TosCH ₂ N=C (0.5 eq)		DBU, DMF, rt, 3 h	II (21)	140																									
C ₇ 					63																										
	<table border="1" data-bbox="616 1871 781 1940"> <thead> <tr> <th>R</th> </tr> </thead> <tbody> <tr> <td>Me</td> </tr> </tbody> </table>	R	Me	1. NaH, THF, 15°, 30 min 2. HCl (0.75 N)	(84)																										
R																															
Me																															
		1. NaH, THF, rt, 1.5 h 2. HCl, pH 1, 1 h	(78)																												
		1. NaH, THF, rt, 2.5 h 2. HCl, pH 1, 1 h	(76)																												

TABLE XI-A.1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TosCHRN=C AND MICHAEL ACCEPTORS (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
<u>R¹</u>	<u>R²</u>	<u>R³</u>		
<i>n</i> -C ₃ F ₇	COMe	H	NaH, DMSO, Et ₂ O, rt, 30 min	(39) 269
Me		H	NaH, DMSO, Et ₂ O, rt, 1 h	(56) 79
	CO ₂ Me	H	<i>n</i> -BuLi, THF, -70 to 0°, 2 h	(34) 79
-(CH ₂) ₄ CO-		H	NaH, DME, -20° to rt, 12 h	(30-50) 270
C ₈ 2,4-Cl ₂ C ₆ H ₃	NO ₂	H	NaH, DMSO, Et ₂ O, 0-5°, 2 h	(38) 272
Ph	NO ₂	H	NaH, DMSO, Et ₂ O, 35°, 1 h	(27) 142
Ph	NO ₂	H	NaH, DMSO, Et ₂ O, 0-5°, 2 h	(55) 272
Ph	NO ₂	H	<i>t</i> -BuOK (2 eq), THF, -80 to -40°, 1 h	(87) 131
Ph	NO ₂	Ph	<i>n</i> -BuLi, THF, -45°, 25 min	(100) 268a
2-C ₄ H ₉ O	COMe	H	NaH, DMSO, Et ₂ O, 20-35°, 15 min	(69) 127
CF ₃	CO ₂ Bu- <i>t</i>	H	NaH, DMSO, Et ₂ O, rt, 30 min	(65) 274
Me		H	NaH, DMSO, Et ₂ O, rt, 3 h	(80) 91, 129
	CO ₂ Et	H	LiN(TMS) ₂ , THF	(61) 91
(<i>E</i>)-EtO ₂ C	CO ₂ Et	H	<i>t</i> -BuOK (2 eq), THF, rt, 2 h	(44) 274a
<i>n</i> -Pr	CO ₂ Et	H	NaH, DMSO, Et ₂ O, rt, 30 min	(74) 275
<i>n</i> -Pr	COEt	H	NaH, DMSO, Et ₂ O, rt, 2.5 h	(40) 276
<i>n</i> -Pr	COEt	H	NaH, DMSO, Et ₂ O, rt, 15 min	(74) 277
	CO ₂ Me	H	<i>t</i> -BuOK (2 eq), THF, 0°, 3.5 h	(70) 63
		TosCH ₂ N=C	DBU, THF, rt, 30 min	 (11) 141
C _{8,9}		TosCH ₂ N=C	NaH, DME, rt, 5 min	 (70) 277a
<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>R⁴</u>	<u>R⁵</u>
Cl	H	H	H	H
H	Cl	H	H	H
H	H	Cl	H	H
Cl	H	Cl	H	H
Cl	H	H	H	Cl
H	Cl	Cl	H	H
H	Cl	H	Cl	H
Cl	H	OH	H	H
Cl	H	OMe	H	H
C _{8,14}		TosCH ₂ N=C	<i>t</i> -BuOK, THF, rt, 1 h	 (75) 277b
<u>R</u>				
Mc				(60)
Ph				(56)
Bn				
C ₉		TosCH ₂ N=C	NaH (2 eq), THF, rt, 3 h	 (24) 139
<u>n</u>				
1				(8)
2				(23)

592

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TABLE XI-A.1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TOSCHRN=C AND MICHAEL ACCEPTORS (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
		NaH (3 eq), DMSO, Et ₂ O, rt, 5 min	 (85)	268a
<u>R¹</u>	<u>R²</u>	<u>R³</u>		
Ph	CN	H	NaH, DMSO, Et ₂ O, 20-35°, 15 min (35)	127
Ph	CN	H	<i>t</i> -BuOK (2 eq), THF, -10°, 10 min (88)	136, 63
Ph	CN	Ph	<i>n</i> -BuLi, THF, rt, 5 d (24)	268a
Ph	CN	Bn	NaH, DMSO, Et ₂ O, rt (80)	69
4-MeC ₆ H ₄	NO ₂	H	NaH, DMSO, Et ₂ O, 0-5°, 2 h (44)	272
4-MeOC ₆ H ₄	NO ₂	H	NaH, DMSO, Et ₂ O, 0-5°, 2 h (58)	272
H		Me	NaH, THF, rt, 15 h (75)	132, 278
	TosCH ₂ N=C (0.5 eq)	DBU, DMF, rt, 3 h		140
	TosCH ₂ N=C	NaH, DME, -35°		279
<u>R¹</u>	<u>R²</u>			
CO ₂ CH ₂ CCl ₃	H		(20)	
COMe	H		(53)	
CO ₂ Et	H		(52)	
COMe	Me		(48)	
COPh	H		(50)	
Tos	H		(4c)	
	TosCH ₂ N=C	<i>t</i> -BuOK, THF, rt, 1 h		277b
<u>R¹</u>	<u>R²</u>	<u>R³</u>		
PhCH=CH	NO ₂	H	<i>t</i> -BuOK (2 eq), THF, -80 to -40°, 1 h (73)	131
H	PhSO ₂ CH=CH	Me	NaH, DMSO, THF, rt, 15 h (64)	132, 133
Ph	COMe	H	NaH, DMSO, Et ₂ O, 20-35°, 15 min (70)	127
Ph	COMe	Ph	<i>n</i> -BuLi, THF, 45°, 1 h (65)	268a
Ph	CO ₂ Me	H	NaH, DMSO, Et ₂ O, 20-35°, 15 min (70)	127
Ph	CO ₂ Me	Ph	NaH, DMSO, Et ₂ O, 20-35°, 15 min (23)	127
Ph	CO ₂ Me	Ph	<i>n</i> -BuLi, THF, rt, 8 d (45)	268a
2,4-MeOC ₆ H ₃	NO ₂	H	NaH, DMSO, Et ₂ O, 0-5°, 2 h (40)	272
<i>n</i> -Bu	CO ₂ Pr- <i>n</i>	H	NaH, DMSO, Et ₂ O, rt, 30 min (74)	275
<i>n</i> -Bu	CO ₂ Pr- <i>n</i>	H	NaH, DMSO, Et ₂ O, rt, 15 min (69)	277
<i>i</i> -Bu	COPr- <i>i</i>	H	NaH, DMSO, Et ₂ O, 45°, 35 min (52)	280
<i>n</i> -C ₆ H ₁₁	CO ₂ Et	H	NaH, DMSO, Et ₂ O, rt, 15 min (95)	281

TABLE XI-A1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TOSCHRN=C AND MICHAEL ACCEPTORS (Continued)

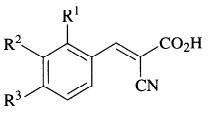
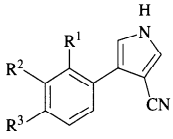
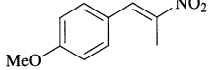
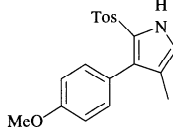
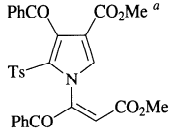
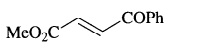
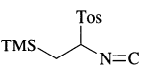
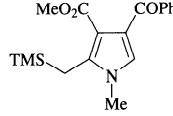
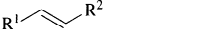
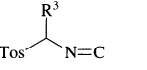
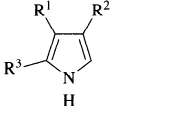
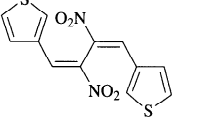
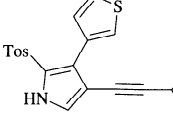
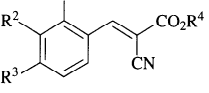
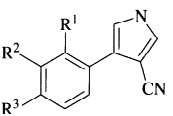
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.																																									
																																													
<table border="1" data-bbox="303 470 512 631"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>Cl</td> <td>H</td> </tr> <tr> <td>F</td> <td>Cl</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>H</td> <td>CN</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Cl	Cl	H	F	Cl	H	H	H	H	H	H	H	H	H	CN	TosCH ₂ N=C TosCH ₂ N=C PhSO ₂ CH ₂ N=C 4-ClC ₆ H ₄ SO ₂ CH ₂ N=C TosCH ₂ N=C	KOH, MeOH, CH ₂ Cl ₂ , 0-5°, 20 min EtONa, CH ₂ Cl ₂ , rt, 3 h KOH, MeOH, CH ₂ Cl ₂ , 0°, 3 h KOH, MeOH, CH ₂ Cl ₂ , 0°, 2 h K ₂ CO ₃ , MeOH, CH ₂ Cl ₂ , 40°, 3 h	(99) (94) (75) (89) (81)	135 137 135 135 135																							
R ¹	R ²	R ³																																											
Cl	Cl	H																																											
F	Cl	H																																											
H	H	H																																											
H	H	H																																											
H	H	CN																																											
C ₁₀ 	TosCH ₂ N=C	DBU, THF, <i>i</i> PrOH, rt, 17 h	 (52)	138																																									
C ₁₁ PhCO—C≡C—CO ₂ Me	TosCH ₂ N=C (0.5 eq)	DBU, DMF, rt, 3 h	 (25)	140																																									
		1. Triton B, THF, 0°, 5 min 2. <i>t</i> -BuOK, MeI, THF, rt, 15 min	 (82)	93																																									
			 (83)																																										
<table border="1" data-bbox="303 1274 512 1664"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>4-ClC₆H₄</td> <td>CO₂Et</td> <td>H</td> </tr> <tr> <td>Ph</td> <td>CO₂Et</td> <td>H</td> </tr> <tr> <td>Ph</td> <td>CO₂Et</td> <td>H</td> </tr> <tr> <td>Ph</td> <td>CO₂Et</td> <td>Ph</td> </tr> <tr> <td>Ph</td> <td>NO₂</td> <td>H</td> </tr> <tr> <td>Me₂NCO</td> <td>COPh</td> <td>TMSCH₂</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>CO₂Et</td> <td>H</td> </tr> <tr> <td>BnOCH₂</td> <td>COMe</td> <td>H</td> </tr> <tr> <td>-(CH₂)₉CO-</td> <td></td> <td>H</td> </tr> <tr> <td>Me</td> <td>CO₂C₈H_{17-n}</td> <td>H</td> </tr> <tr> <td><i>n</i>-C₅H₁₁</td> <td>CO₂Bu-<i>n</i></td> <td>H</td> </tr> <tr> <td><i>n</i>-C₅H₁₁</td> <td>CO₂Bu-<i>n</i></td> <td>H</td> </tr> <tr> <td><i>n</i>-C₇H₁₅</td> <td>CO₂Et</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	4-ClC ₆ H ₄	CO ₂ Et	H	Ph	CO ₂ Et	H	Ph	CO ₂ Et	H	Ph	CO ₂ Et	Ph	Ph	NO ₂	H	Me ₂ NCO	COPh	TMSCH ₂	4-MeOC ₆ H ₄	CO ₂ Et	H	BnOCH ₂	COMe	H	-(CH ₂) ₉ CO-		H	Me	CO ₂ C ₈ H _{17-n}	H	<i>n</i> -C ₅ H ₁₁	CO ₂ Bu- <i>n</i>	H	<i>n</i> -C ₅ H ₁₁	CO ₂ Bu- <i>n</i>	H	<i>n</i> -C ₇ H ₁₅	CO ₂ Et	H	NaH, DMSO, Et ₂ O, rt, 2 h NaH, DMSO, Et ₂ O, rt, 15 min NaH, DMSO, Et ₂ O, rt, 2 h <i>n</i> -BuLi, THF, rt, 8 d <i>t</i> -BuOK (2 eq), THF, -80 to -40°, 1 h Triton B, THF, rt, 15 min NaH, DMSO, Et ₂ O, rt, 2 h NaH, DMSO, Et ₂ O, 20-35°, 15 min NaH, DME, -20° to rt, 1 h NaH, DMSO, Et ₂ O, rt, 30 min NaH, DMSO, Et ₂ O, rt, 30 min NaH, DMSO, Et ₂ O, rt, 15 min NaH, DMSO, Et ₂ O, rt, 30 min	(83) (60) (71) (43) (75) (90) (72) (83) (30-50) (91) (34) (34) (80)	282 271 282 268a 131 93 282 33 270 275, 271 275 277 281
R ¹	R ²	R ³																																											
4-ClC ₆ H ₄	CO ₂ Et	H																																											
Ph	CO ₂ Et	H																																											
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4-MeOC ₆ H ₄	CO ₂ Et	H																																											
BnOCH ₂	COMe	H																																											
-(CH ₂) ₉ CO-		H																																											
Me	CO ₂ C ₈ H _{17-n}	H																																											
<i>n</i> -C ₅ H ₁₁	CO ₂ Bu- <i>n</i>	H																																											
<i>n</i> -C ₅ H ₁₁	CO ₂ Bu- <i>n</i>	H																																											
<i>n</i> -C ₇ H ₁₅	CO ₂ Et	H																																											
	TosCH ₂ N=C	DBU, THF, rt, 30 min	 (40)	141																																									
				135																																									
<table border="1" data-bbox="303 1928 512 2061"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H</td> <td>H</td> <td>Et</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Et</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Et</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>MeO</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Cl	H	H	Et	H	H	H	Et	H	H	H	Et	H	MeO	MeO	H	TosCH ₂ N=C TosCH ₂ N=C 4-ClC ₆ H ₄ SO ₂ CH ₂ N=C TosCH ₂ N=C	EtONa, EtOH, CH ₂ Cl ₂ , 0-3°, 1 h NaH, DME, rt, 1 h NaOMe, MeOH, CH ₂ Cl ₂ , 0°, 3 h KOH, DME, rt, 2 h	(98) (89) (89) (92)																						
R ¹	R ²	R ³	R ⁴																																										
Cl	H	H	Et																																										
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H	MeO	MeO	H																																										

TABLE XI-A1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TosCHRN=C AND MICHAEL ACCEPTORS (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH ₂ N=C	DBU, MeCN, 0°, 30 min	(80)	283
C ₁₃ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-35°, 15 min	(—)	284
	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 20-35°, 15 min		127
C ₁₃₋₁₄ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 4 h		134
C ₁₃₋₁₉ 	TosCH ₂ N=C	<i>t</i> -BuOK, THF, rt, 30 min	(23)	285
		NaH, DMSO, Et ₂ O, rt, 4 h	(6)	
		NaH, DMSO, Et ₂ O, 0°, 1.5 h	(35)	
			(56)	
			(52)	
R				
Me				
Et				
CN				
CO ₂ Me				
COMe				
COPh				
C ₁₄ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 30 min	(25)	286
	TosCH ₂ N=C	NaOH, EtOH, 0°, 1 h	(60)	136
		1. Triton B, THF, rt, 30 min 2. <i>t</i> -BuOK, MeI, THF, rt, 30 min	(77)	93
R ¹	R ²	R ³		
<i>n</i> -C ₆ H ₁₃	CO ₂ C ₅ H _{11-n}	H	NaH, DMSO, Et ₂ O, rt, 15-30 min	(28) 277, 275
Ph	COPh	H	NaH, DMSO, Et ₂ O, 20-35°, 15 min	(70) 127
Ph	COPh	H	Triton B (2 eq), THF, rt, 15 min	(88) 136
Ph	COPh	Ph	<i>n</i> -BuLi, THF, rt, 3 h	(80) 268a
Ph	COPh	CH ₂ TMS	<i>t</i> -BuOK, THF, rt, 15 min	(79) 93
Ph	COPh	Me	NaH, DMSO, Et ₂ O, rt	(83) 69
Ph	COPh	CH ₂ =CHCH ₂	NaH, DMSO, Et ₂ O, rt	(78) 69
Ph	COPh	Bn	NaH, DMSO, Et ₂ O, rt	(83) 69

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TABLE XI-A1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TOSCHRN=C AND MICHAEL ACCEPTORS (Continued)

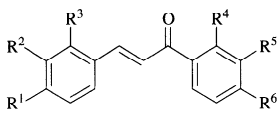
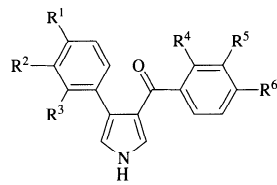
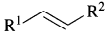
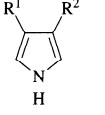
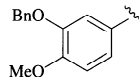
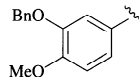
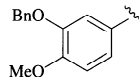
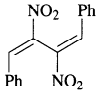
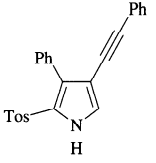
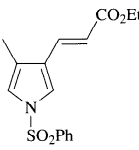
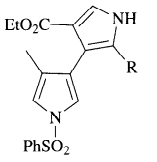
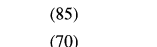
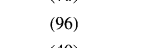
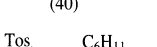
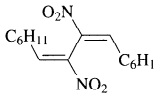
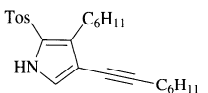
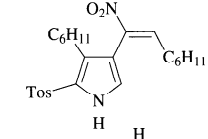
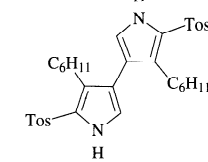
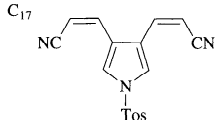
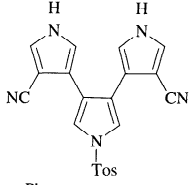
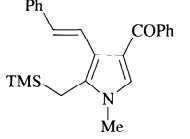
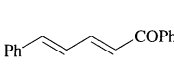
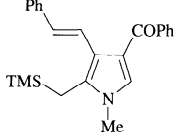
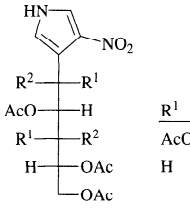
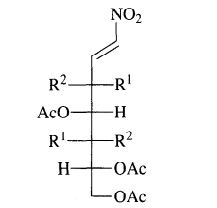
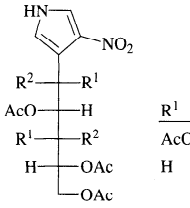
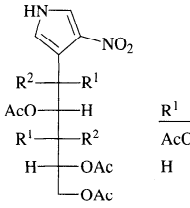
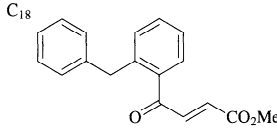
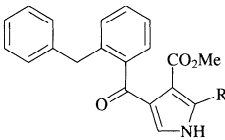
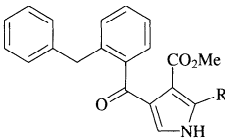
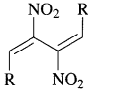
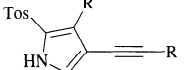
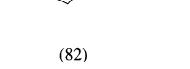
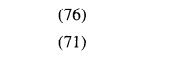
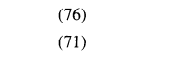
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TABLE XI-A1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TosCHRN=C AND MICHAEL ACCEPTORS (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{Tos}-\text{CH}(\text{R})-\text{N}=\text{C}$ R _____ H Me $\text{CH}_2=\text{CHCH}_2$ TMSCH_2	NaI, $(\text{TMS})_2\text{NH}$	 (85)	91, 129
			 (70)	91
			 (96)	91, 129
			 (40)	91
	TosCH ₂ N=C	DBU, THF, rt, 30 min	 (58) +	141
			 (12) +	
			 (9)	
	TosCH ₂ N=C	NaH, DMF, 0-5°	 (66)	130
			 (84)	93
	$\text{TMS}-\text{CH}_2-\text{CH}(\text{Tos})-\text{N}=\text{C}$	1. <i>t</i> -BuOK, THF, rt, 10 min 2. MeI, THF, NaOH (50%), TBAI, rt, 30 min	 (84)	93
			 (50)	288
	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, 0°, 2 h	 (51)	288
			 (50)	288
	$\text{Tos}-\text{CH}(\text{R})-\text{N}=\text{C}$	NaH, DMSO, Et ₂ O, rt, 1 h	 (41)	289
			 (46)	289
	TosCH ₂ N=C	DBU, THF, rt, 30 min	 (82)	141
			 (76)	
			 (71)	
			 (71)	

602

603

TABLE XI-A1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TOSCHRN=C AND MICHAEL ACCEPTORS (Continued)

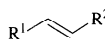
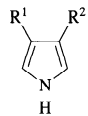
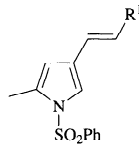
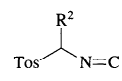
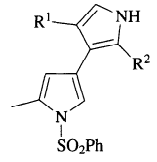
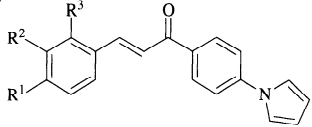
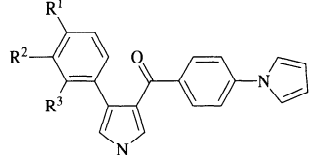
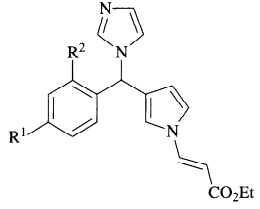
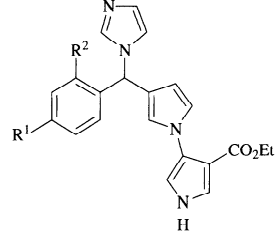
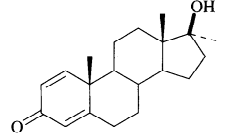
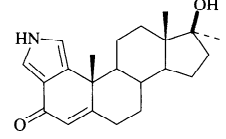
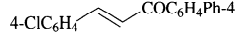
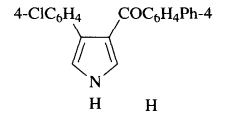
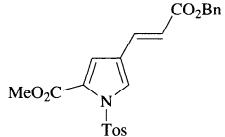
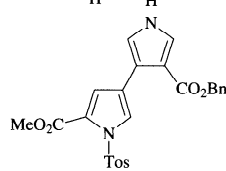
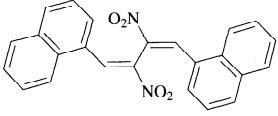
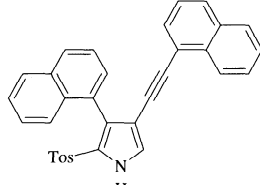
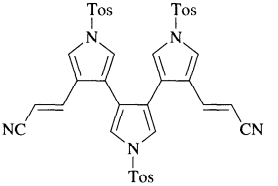
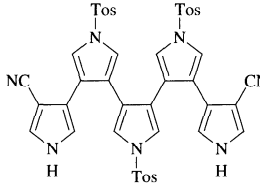
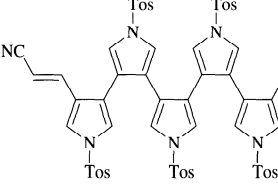
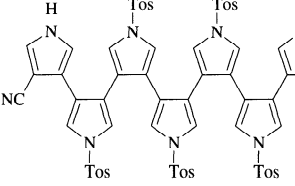
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.																		
C ₁₈₋₁₉ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt	 (42) (52)	275 287																		
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R ¹	R ²																					
<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₇ H ₁₅ CO ₂																					
4-ClC ₆ H ₄	1-C ₁₀ H ₇ CO																					
 SO ₂ Ph	 Tos-CH(R ²)-N=C	 SO ₂ Ph	(74) (72) (95)	133, 278 133, 278 133																		
<table border="1" style="margin-left: 20px;"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>CO₂Bu-<i>t</i></td> <td>H</td> </tr> <tr> <td>SO₂Ph</td> <td>H</td> </tr> <tr> <td>SO₂Ph</td> <td>Et</td> </tr> </tbody> </table>	R ¹	R ²	CO ₂ Bu- <i>t</i>	H	SO ₂ Ph	H	SO ₂ Ph	Et		NaH, THF, rt, 1.5 h NaH, THF, DMSO, rt NaH, DMSO, (TMS) ₂ NH, rt												
R ¹	R ²																					
CO ₂ Bu- <i>t</i>	H																					
SO ₂ Ph	H																					
SO ₂ Ph	Et																					
C ₁₉ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt	 (23) (54) (93) (33) (57)	287																		
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Cl	H	Cl																				
Cl	Cl	H																				
 CO ₂ Et	TosCH ₂ N=C	NaH, DMF, 0°	 (52) (36) (19) (62)	290																		
<table border="1" style="margin-left: 20px;"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> </tr> <tr> <td>Cl</td> <td>H</td> </tr> <tr> <td>Cl</td> <td>Cl</td> </tr> </tbody> </table>	R ¹	R ²	H	H	Me	H	Cl	H	Cl	Cl												
R ¹	R ²																					
H	H																					
Me	H																					
Cl	H																					
Cl	Cl																					
C ₂₀ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O	 (25)	291																		
C ₂₁ 	TosCH ₂ N=C	NaH, DMSO, Et ₂ O, rt, 5 min	 (54)	287																		
C ₂₃  MeO ₂ C Tos	TosCH ₂ N=C	LiN(TMS) ₂ , THF, rt, 15 min	 (72)	132																		

TABLE XI-A1. PYRROLES FROM TOSMIC OR TOSMIC HOMOLOGS TOSCHRN=C AND MICHAEL ACCEPTORS (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
	TosCH ₂ N=C	DBU, THF, rt, 30 min	 (59)	141
	TosCH ₂ N=C	NaH, DMF, 0-5°	 (83)	130
	TosCH ₂ N=C	NaH, DMF, 0-5°	 (73)	130

^a Since aryl groups are more strongly directing than ester groups, it seems likely that the positions of the aryl and ester groups at C-3 and C-4 should be exchanged. The reported spectral data are consistent with either structure.

TABLE XI-A2. PYRROLES FROM TOSMIC HOMOLOGS TOSC(=CR₂)N=C AND MICHAEL ACCEPTORS

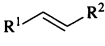
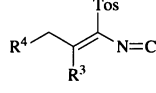
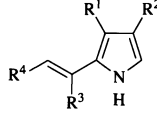
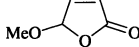
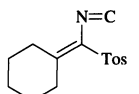
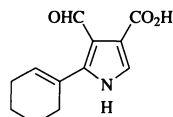
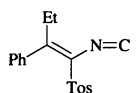
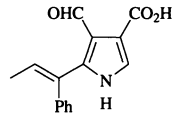
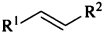
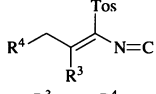
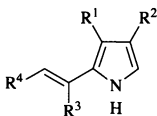
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.																														
																																		
<table border="1" style="margin-left: 20px;"> <tr> <th>R¹</th> <th>R²</th> </tr> <tr> <td>CN</td> <td>CN</td> </tr> <tr> <td>CN</td> <td>CN</td> </tr> <tr> <td>H</td> <td>COMe</td> </tr> <tr> <td>H</td> <td>CO₂Me</td> </tr> <tr> <td>H</td> <td>COMe</td> </tr> <tr> <td>H</td> <td>CO₂Me</td> </tr> </table>	R ¹	R ²	CN	CN	CN	CN	H	COMe	H	CO ₂ Me	H	COMe	H	CO ₂ Me	<table border="1" style="margin-left: 20px;"> <tr> <th>R³</th> <th>R⁴</th> </tr> <tr> <td>(CH₂)₄</td> <td></td> </tr> <tr> <td>Ph</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> </tr> <tr> <td>(CH₂)₄</td> <td></td> </tr> <tr> <td>(CH₂)₄</td> <td></td> </tr> <tr> <td>(CH₂)₄</td> <td></td> </tr> </table>	R ³	R ⁴	(CH ₂) ₄		Ph	Me	Me	H	Me	H	(CH ₂) ₄		(CH ₂) ₄		(CH ₂) ₄		<i>t</i> -BuOK (2 eq), THF, -60° to rt, 3 h <i>t</i> -BuOK (2 eq), THF, -90°, stand 45 min <i>t</i> -BuOK, THF, -60 to 20°, 1 h <i>t</i> -BuOK, THF, -60 to 20°, 1 h <i>t</i> -BuOK, THF, -60 to 20°, 1 h <i>t</i> -BuOK, THF, -60 to 20°, 1 h Triton B (1.9 eq), THF, rt, 1.5 h <i>t</i> -BuOK (2 eq), THF, -70°, stand 30 min	(46) (81) (88) (90) (96) (83) (98) (79)	63 63 128 128 128 128 63 63
R ¹	R ²																																	
CN	CN																																	
CN	CN																																	
H	COMe																																	
H	CO ₂ Me																																	
H	COMe																																	
H	CO ₂ Me																																	
R ³	R ⁴																																	
(CH ₂) ₄																																		
Ph	Me																																	
Me	H																																	
Me	H																																	
(CH ₂) ₄																																		
(CH ₂) ₄																																		
(CH ₂) ₄																																		
		1. <i>t</i> -BuOK (3 eq), THF, -70 to -55°, 1.5 h 2. HCl (0.1 N), -60 to -10°	 (66)	63																														
		1. <i>t</i> -BuOK (2 eq), THF, -90 to -40°, 0.5 h 2. HCl (0.1 N), -40°	 (55)	63																														
																																		
<table border="1" style="margin-left: 20px;"> <tr> <th>R¹</th> <th>R²</th> </tr> <tr> <td>Me</td> <td>CO₂Me</td> </tr> <tr> <td>CO₂Me</td> <td>COMe</td> </tr> <tr> <td>CO₂Me</td> <td>CO₂Me</td> </tr> </table>	R ¹	R ²	Me	CO ₂ Me	CO ₂ Me	COMe	CO ₂ Me	CO ₂ Me	<table border="1" style="margin-left: 20px;"> <tr> <th>R³</th> <th>R⁴</th> </tr> <tr> <td>(CH₂)₃</td> <td></td> </tr> <tr> <td>(CH₂)₄</td> <td></td> </tr> <tr> <td>(CH₂)₄</td> <td></td> </tr> </table>	R ³	R ⁴	(CH ₂) ₃		(CH ₂) ₄		(CH ₂) ₄		<i>t</i> -BuOK, THF, -60 to 20°, 1 h Triton B, THF, 20-30°, 45 min <i>t</i> -BuOK (2 eq), THF, -70°, stand 2 h	(84) (83) (92) ^a	128 63 63														
R ¹	R ²																																	
Me	CO ₂ Me																																	
CO ₂ Me	COMe																																	
CO ₂ Me	CO ₂ Me																																	
R ³	R ⁴																																	
(CH ₂) ₃																																		
(CH ₂) ₄																																		
(CH ₂) ₄																																		

TABLE XI-A2. PYRROLES FROM TOSMIC HOMOLOGS TOSC(=CR₂)N=C AND MICHAEL ACCEPTORS (Continued)

	Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.																								
C ₇	<table border="1"> <tr><th>R¹</th><th>R²</th></tr> <tr><td>CH₂=C(OMe)</td><td>CO₂Me</td></tr> <tr><td>MeC(NOMe)</td><td>CO₂Me</td></tr> <tr><td colspan="2"><i>E/Z</i> = 5:1</td></tr> <tr><td>MeC(NOMe)</td><td>CO₂Me</td></tr> <tr><td colspan="2"><i>E/Z</i> = 5:1</td></tr> </table>	R ¹	R ²	CH ₂ =C(OMe)	CO ₂ Me	MeC(NOMe)	CO ₂ Me	<i>E/Z</i> = 5:1		MeC(NOMe)	CO ₂ Me	<i>E/Z</i> = 5:1		<table border="1"> <tr><th>R³</th><th>R⁴</th></tr> <tr><td>(CH₂)₄</td><td></td></tr> <tr><td>(CH₂)₄</td><td></td></tr> <tr><td>Ph</td><td>Me</td></tr> </table>	R ³	R ⁴	(CH ₂) ₄		(CH ₂) ₄		Ph	Me	<i>t</i> -BuOK (2 eq), THF, -30°, stand 3 h <i>t</i> -BuOK (2 eq), THF, -45° to rt, 1 h <i>t</i> -BuOK (2 eq), THF, -15°; rt, 4.5 h	(28) (92) <i>E/Z</i> = 5:1 (87) <i>E/Z</i> = 5:1	63 63 63				
R ¹	R ²																												
CH ₂ =C(OMe)	CO ₂ Me																												
MeC(NOMe)	CO ₂ Me																												
<i>E/Z</i> = 5:1																													
MeC(NOMe)	CO ₂ Me																												
<i>E/Z</i> = 5:1																													
R ³	R ⁴																												
(CH ₂) ₄																													
(CH ₂) ₄																													
Ph	Me																												
809			1. NaH, DME, -20° to rt, 2 h 2. MeI, PTC 3. HCl (1.5 N)		63																								
			1. NaH, DME, -20°, 3 h 2. MeI, PTC 3. HCl (1.5 N)		63																								
C ₈			<i>t</i> -BuOK, THF, -60 to 20°		128																								
	<table border="1"> <tr><th>R¹</th><th>R²</th></tr> <tr><td>3-C₅H₄N</td><td>CN</td></tr> <tr><td>Ph</td><td>NO₂</td></tr> <tr><td>Ph</td><td>NO₂</td></tr> <tr><td>CO₂Et</td><td>CO₂Et</td></tr> </table>	R ¹	R ²	3-C ₅ H ₄ N	CN	Ph	NO ₂	Ph	NO ₂	CO ₂ Et	CO ₂ Et	<table border="1"> <tr><th>R³</th><th>R⁴</th></tr> <tr><td>(CH₂)₄</td><td></td></tr> <tr><td>Me</td><td>H</td></tr> <tr><td>(CH₂)₄</td><td></td></tr> <tr><td>Ph</td><td>Me</td></tr> </table>	R ³	R ⁴	(CH ₂) ₄		Me	H	(CH ₂) ₄		Ph	Me	<i>t</i> -BuOK (2 eq), THF, -55° to rt, 1.5 h <i>t</i> -BuOK (2 eq), THF, -80 to -40°, 1 h <i>t</i> -BuOK (2 eq), THF, -80 to -40°, 1 h <i>t</i> -BuOK (2 eq), THF, -50°; stand 30 min	(86) (84) (93) (81)	63 131 131 63				
R ¹	R ²																												
3-C ₅ H ₄ N	CN																												
Ph	NO ₂																												
Ph	NO ₂																												
CO ₂ Et	CO ₂ Et																												
R ³	R ⁴																												
(CH ₂) ₄																													
Me	H																												
(CH ₂) ₄																													
Ph	Me																												
		(CH ₂) ₄	NaH, <i>t</i> -BuOK or BuLi, -70° to rt	(0)	63																								
		(CH ₂) ₄	NaH, <i>t</i> -BuOK or BuLi, -70° to rt	(0)	63																								
C ₉	Ph	CN	(CH ₂) ₄	<i>t</i> -BuOK (2 eq), THF, -45°; rt, 3 h	(74)	63																							
C ₁₀	Ph	CO ₂ Me	(CH ₂) ₄	<i>t</i> -BuOK, THF, -60 to 20°, 1 h	(95)	128																							
	(<i>E</i>)-PhCH=CH	NO ₂	Me	H	(78)	131																							
	(<i>E</i>)-PhCH=CH	NO ₂	(CH ₂) ₄		(71)	131																							
C ₁₁			Triton B, THF, 20-30°, 20 min		63																								
	<table border="1"> <tr><th>R¹</th><th>R²</th></tr> <tr><td>2-C₄H₃O</td><td>2-C₄H₃OCO</td></tr> <tr><td>2-C₄H₃S</td><td>2-C₄H₃SCO</td></tr> <tr><td>CO₂Me</td><td>PhCO</td></tr> </table>	R ¹	R ²	2-C ₄ H ₃ O	2-C ₄ H ₃ OCO	2-C ₄ H ₃ S	2-C ₄ H ₃ SCO	CO ₂ Me	PhCO	<table border="1"> <tr><th>R³</th><th>R⁴</th></tr> <tr><td>(CH₂)₃</td><td></td></tr> <tr><td>(CH₂)₄</td><td></td></tr> <tr><td>Me</td><td>H</td></tr> </table>	R ³	R ⁴	(CH ₂) ₃		(CH ₂) ₄		Me	H	<i>t</i> -BuOK, THF, -60 to 20°, 1 h <i>t</i> -BuOK, THF, -60 to 20°, 1 h Triton B, THF, rt, 30 min	<table border="1"> <tr><th>R⁵</th><td></td></tr> <tr><td>H</td><td>(93)</td></tr> <tr><td>H</td><td>(85)</td></tr> <tr><td>H</td><td>(92)</td></tr> </table>	R ⁵		H	(93)	H	(85)	H	(92)	128 128 63
R ¹	R ²																												
2-C ₄ H ₃ O	2-C ₄ H ₃ OCO																												
2-C ₄ H ₃ S	2-C ₄ H ₃ SCO																												
CO ₂ Me	PhCO																												
R ³	R ⁴																												
(CH ₂) ₃																													
(CH ₂) ₄																													
Me	H																												
R ⁵																													
H	(93)																												
H	(85)																												
H	(92)																												

809

609

TABLE XI-A2. PYRROLES FROM TOSMIC HOMOLOGS TOSC(=CR₂)N=C AND MICHAEL ACCEPTORS (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
<u>R¹</u>	<u>R²</u>	<u>R³</u> <u>R⁴</u>	<u>R⁵</u>	
CO ₂ Me	PhCO	(CH ₂) ₄	H (83)	63
CO ₂ Me	PhCO	Ph Me	H (85)	63
C ₁₂	CO ₂ Me	(CH ₂) ₄	H (60)	143
	NO ₂	Me H	H (89)	131
	NO ₂	(CH ₂) ₄	H (85)	131
	NO ₂	(CH ₂) ₄	Me (67)	146
	NO ₂	Ph H	H (80)	131
	COMe	Ph H	H (92)	128
	COMe	(CH ₂) ₅	Me (87)	128
	CO ₂ Me	(CH ₂) ₄	Me (90)	128, 80
C ₁₃ 2-C ₄ H ₃ O	PhCO	(CH ₂) ₅	H (89)	128
C ₁₅ Ph	PhCO	Me H	H (95)	128
Ph	PhCO	(CH ₂) ₃	H (95)	128
Ph	PhN=CH	(CH ₂) ₅	H (70)	80
C ₁₆ PhCO	PhCO	(CH ₂) ₄	H (84)	63
PhCO	PhCO	Ph H	H (70)	63
PhCO	PhCO	Ph Me	H (75)	63
Ph	TsN=CH	(CH ₂) ₄	H (34) ^b	80
C ₁₇ Ph		(CH ₂) ₄	H (96)	128
<u>R¹</u>	<u>R²</u>	<u>R³</u> <u>R⁴</u>	<u>R⁵</u>	
	PhCO	Me H	H (96)	128
	PhCO	(CH ₂) ₃	Me (84)	128
	PhCO	(CH ₂) ₄	H (91)	128, 80
	PhCO	(CH ₂) ₅	Me (87)	128
	PhCO	(CH ₂) ₆	Me (83)	128
	PhCO	(CH ₂) ₁₀	Me (82)	128

^a The same pyrrole was obtained in 90% yield from dimethyl maleate instead of dimethyl fumarate.

^b An imidazole (34%) was also formed by reaction with the carbon-nitrogen double bond.

TABLE XI-B. PYRROLES FROM 1-ISOCYANO-1-TOSYLALKENES AND MICHAEL DONORS

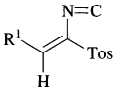


Substrate	Michael Donor	Conditions	Product(s) and Yield(s) (%)	Refs.			
							
	<table border="0"> <tr> <td><u>R¹</u></td> <td><u>R²</u></td> <td><u>R³</u></td> </tr> </table>	<u>R¹</u>	<u>R²</u>	<u>R³</u>			
<u>R¹</u>	<u>R²</u>	<u>R³</u>					
C ₁₄ <i>t</i> -Bu	H	NO ₂	<i>t</i> -BuOK, DME, rt, 15 min	(91) 142			
<i>n</i> -Bu	MeCO	CO ₂ Et	<i>t</i> -BuOK, EtOH, rt, 1 h	(62) 136			
<i>n</i> -Bu	PhCO	Me	1. <i>t</i> -BuOK, DME, rt, 1 h 2. MeOH, rt, 5 min	(33) 136			
C ₁₆ 2,3-Cl ₂ C ₆ H ₃	EtO ₂ C	CN	NaOH, EtOH, rt, 1 h	(93) 136			
4-ClC ₆ H ₄	H	NO ₂	<i>t</i> -BuOK, DME, rt, 15 min	(86) 142			
Ph	H	NO ₂	<i>t</i> -BuOK, DME, rt, 15 min	(94) 142			
Ph	H	CN	<i>t</i> -BuOK, DME, rt, 15 min	(0) 136			
Ph	H	CO ₂ Et	<i>t</i> -BuOK, DME, rt, 15 min	(0) 136			
Ph	EtO ₂ C	CN	Na, EtOH, rt, 30 min	(99) 136			
Ph	MeCO	COMe	NaOH, MeOH, rt, 2.5 h	(86) 136			
Ph	MeCO	CO ₂ Et	Na, EtOH, rt, 30 min	(92) 136			
Ph	EtO ₂ C	CO ₂ Et	Na, EtOH, rt, 30 min	(70) 136			
Ph	H	COPh	<i>t</i> -BuOK, DME, rt, 1 h	(57) 136			
Ph	PhCO	Me	1. <i>t</i> -BuOK, DME, rt, 1 h 2. MeOH, rt, 5 min	(73) 136			
Ph	EtO ₂ C	Ph	<i>t</i> -BuOK, DME, rt, 1 h	(57) 136			
Ph	PhCO	COPh	1. NaOH, MeOH, reflux, 5 min 2. rt, 3 h	(61) 136			
C ₁₇ 4-MeOC ₆ H ₄	H	NO ₂	<i>t</i> -BuOK, DME, rt, 15 min	(88) 142			

TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES



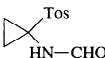
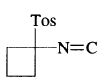

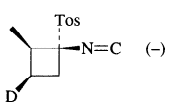

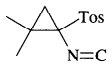
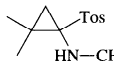
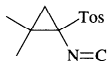
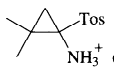
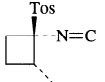

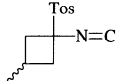

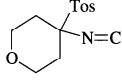

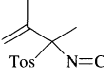

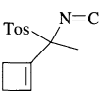

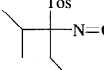

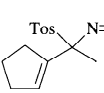

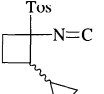

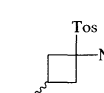

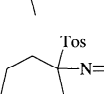

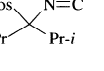

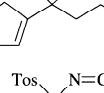



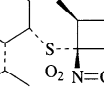


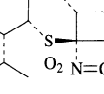

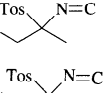

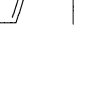

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	HCl (37%), THF, -10°, 5 min	 (0),  (79) ^a	99
C ₁₂ 	H ₂ SO ₄ (50%), sulfolane, 20 to 100°, 2 h	 (84)	148
C ₁₃  (-)	H ₂ SO ₄ (50%), sulfolane, 20 to 100°, 2 h	 (2 <i>R</i> ,3 <i>R</i>)-(+), (97)	245
	HCl (37%), THF, -10°, 5 min	 (84) ^a	102
	1. HCl (37%), MeOH, -10°, 1 h 2. rt, 20 h	 (92) ^a	102
	H ₂ SO ₄ (50%), sulfolane, 20 to 100°, 2 h	 (88)	148
	H ₂ SO ₄ (50%), sulfolane, 20 to 100°, 2 h	 (88)	148
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (16) ^b	98

TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	HCl (37%), Et ₂ O rt, <5 min	 (51)	103
C ₁₄ 	HCl (37%), Et ₂ O rt, <5 min	 (69)	103
	H ₂ SO ₄ (50%), sulfolane	 (20) ^b Z:E = 3:1	247
C ₁₅ 	HCl (37%), Et ₂ O rt, <5 min	 (91)	103
	H ₂ SO ₄ (50%), sulfolane, rt, 10 min	 (30)	247
	H ₂ SO ₄ (50%), sulfolane, 120°, 3 h	 (75)	247
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (51) ^b	98
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (47) ^b	98
C ₁₆ 	HCl (37%), Et ₂ O rt, <5 min	 (90)	103
	HCl (37%), Et ₂ O rt, <5 min	 (93)	103
	H ₂ SO ₄ (50%), sulfolane, 20 to 80°, 2 h	 (S)-(-), 43% ee (87)	39
(1 <i>S</i> ,2 <i>S</i>)	H ₂ SO ₄ (50%), sulfolane, 50°, 0.5 h	 (S)-(-), 62% ee (44)	39
	H ₂ SO ₄ (50%), sulfolane, 50°, 0.5 h	 (R)-(+), 54% ee (60)	39
C ₁₇ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (58) ^b	98
	HCl (37%), Et ₂ O rt, <5 min	 (67)	103

614

615

TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

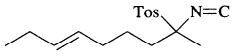
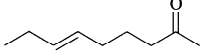
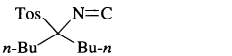
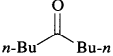
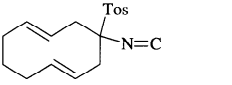
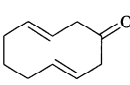
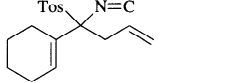
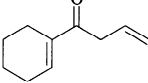
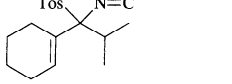
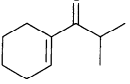
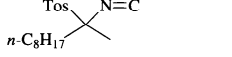
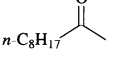
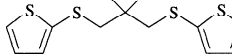
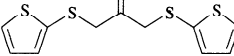
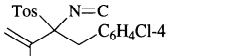
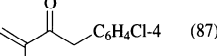
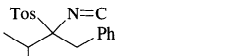
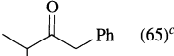
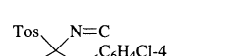
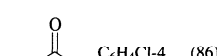
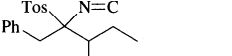
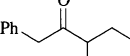
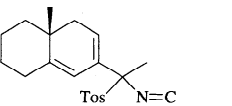
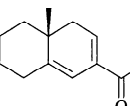
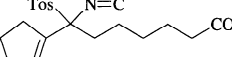
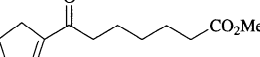
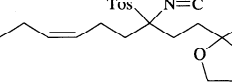
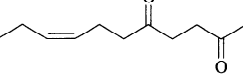
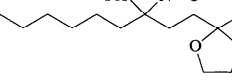
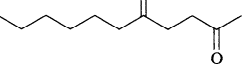
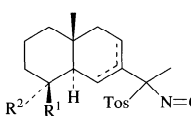
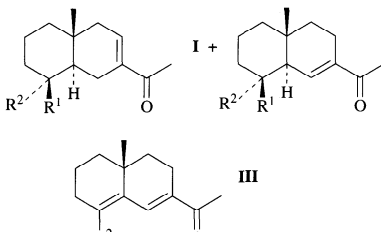
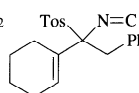
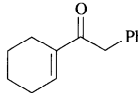
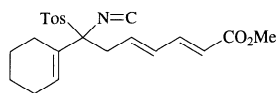
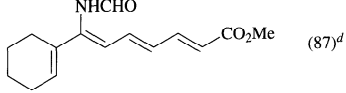
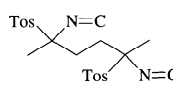
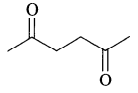
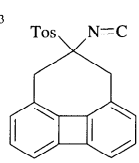
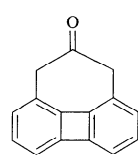
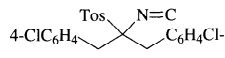
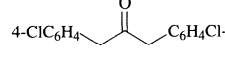
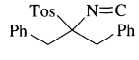
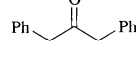
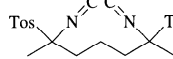
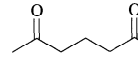
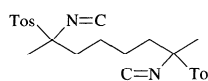
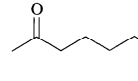
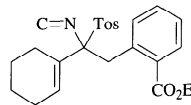
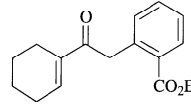
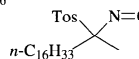
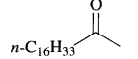
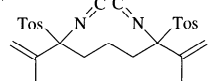
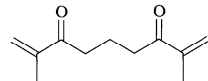
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
916		HCl (37%), CH ₂ Cl ₂ , 0°, 10 h	 (90)	97
		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 5 min	 (69) ^b	98
		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 5 min	 (54)	149
		HCl (37%), Et ₂ O, rt, <5 min	 (87)	103
		HCl (37%), Et ₂ O, rt, <5 min	 (90)	103
		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 5 min	 (80) ^c	98
		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 5 min	 (—)	246
		HCl (37%), Et ₂ O, rt, <5 min	 (87)	103
		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 5 min	 (65) ^c	98
		HCl (37%), Et ₂ O, rt, <5 min	 (86)	103
617		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 5 min	 (41) ^c	98
		HCl (37%), Et ₂ O, rt, 10 min	 (44)	235
		HCl (37%), Et ₂ O, rt, <5 min	 (67)	103
		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 15 min	 (100)	152
		HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 15 min	 (100)	152

TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₂₁₋₂₄ 			235												
<table border="0"> <tr> <td><u>R¹</u></td> <td><u>R²</u></td> </tr> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>OH</td> <td>H</td> </tr> <tr> <td>OH</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>OH</td> </tr> <tr> <td>OTMS</td> <td>H</td> </tr> </table>	<u>R¹</u>	<u>R²</u>	H	H	OH	H	OH	Me	Me	OH	OTMS	H	HCl (37%), Et ₂ O rt, 10 min HClO ₄ (40%), Et ₂ O, reflux 45 min " " "	(I + II) (58), I:II = 10:1 I (5) + II (46) + III (3) I (6) + II (55) + III (6) II (62) + III R ² = Me (3) I R ¹ = OH (81)	
<u>R¹</u>	<u>R²</u>														
H	H														
OH	H														
OH	Me														
Me	OH														
OTMS	H														
C ₂₂ 	HCl (37%), Et ₂ O rt, <5 min	 (86)	103												
	HCl (37%), Et ₂ O rt, <5 min	 (87) ^d	103												
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 15 min	 (66)	100												
C ₂₃ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (17) ^b	111												
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (56) ^b	98												
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (72) ^b	98												
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 15 min	 (82)	100												
C ₂₄ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 15 min	 (82)	100												
C ₂₅ 	HCl (37%), Et ₂ O rt, <5 min	 (86)	103												
C ₂₆ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (63) ^c	98												
C ₂₇ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	 (76)	103												

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TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 15 min	(75) ^c	152
	H ₂ SO ₄ (2 N), MeOH	(75) ^c	151
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 2 h	(67) ^c	237
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	(85)	238
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 5 min	(85)	239
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 15 min	(95)	100
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 2 h	(—)	237
	HCl (37%), Et ₂ O, rt, 5 min	(71)	103
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 15 min	(93)	100
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 10 min	(29)	101
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 2 min	(97)	101
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O rt, 2 min	(68)	101
	H ₂ SO ₄ (2 N), MeOH	(2 <i>R</i> ,6 <i>R</i> ,8 <i>S</i>) (67) ^e	151
	H ₂ SO ₄ (2 N), MeOH	(2 <i>S</i> ,6 <i>R</i>) (55) ^{b,e}	151
	HCl (37%), CH ₂ Cl ₂ , rt, 2 h	(70) ^c	240

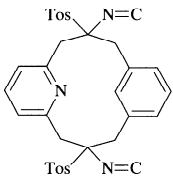
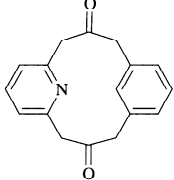
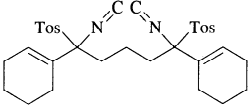
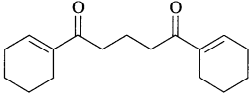
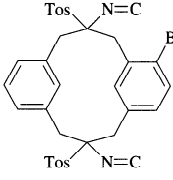
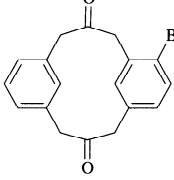
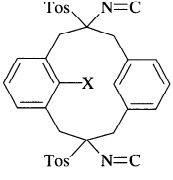
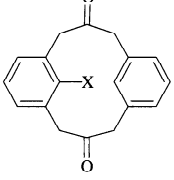
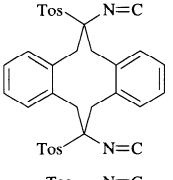
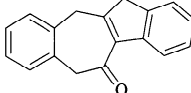
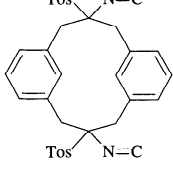
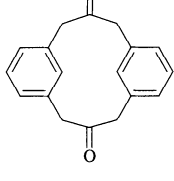
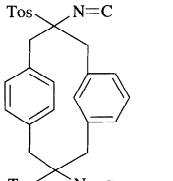
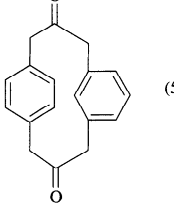
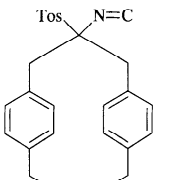
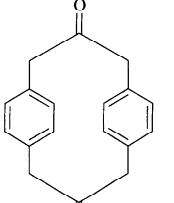
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TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₀ 	HCl (6 N), CH ₂ Cl ₂ , Et ₂ O, 0°, 1.5 h	(60)	101
	HClO ₄ (40%), Et ₂ O, 30°, 10 min	$\frac{X}{\text{Br}}$ (80) Cl (50)	101
	HClO ₄ (40%), Et ₂ O, CH ₂ Cl ₂ , rt, 3 min	(90)	101
	HCl (5 N), CH ₂ Cl ₂ , Et ₂ O, rt, 4 h	(90)	101
	HCl (8 N), CH ₂ Cl ₂ , Et ₂ O, rt, 10 min	(50)	101
	HCl (6 N), CH ₂ Cl ₂ , rt, 45 min	(90)	45
C ₃₁ 	HCl (37%), Et ₂ O, rt, 5 min	(89)	103
	HCl (6 N), CH ₂ Cl ₂ , Et ₂ O, 0°, 1.5 h	(60)	101
	HCl (8 N), C ₆ H ₆ , rt, 3 h	(38)	101
C ₃₂ 	HCl (37%), CH ₂ Cl ₂ , rt, 30 min	$\frac{X}{\text{O}}$ time O 5 min (39) ^f S 30 min (41) ^f	92

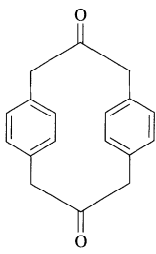
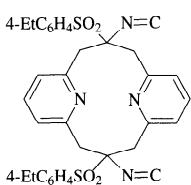
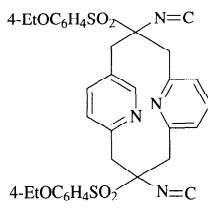
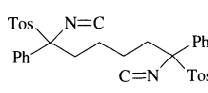
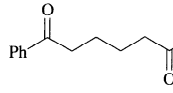
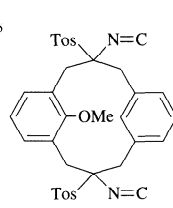
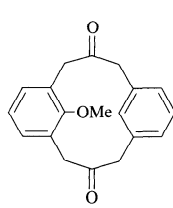
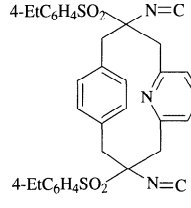
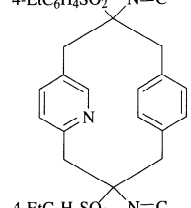
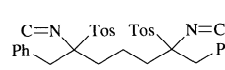
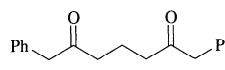
TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₃₃ 	HCl (37%), CH ₂ Cl ₂ , rt, 0.5 h	 (43) ^c	92										
	HCl (37%), Et ₂ O, rt, 5 min	 (90)	103										
C ₃₄ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O	 (59) ^b	193										
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O	 <table border="0" style="margin-left: 20px;"> <tr><td>X</td><td></td></tr> <tr><td>F</td><td>(68)^b</td></tr> <tr><td>Cl</td><td>(57)^b</td></tr> <tr><td>Br</td><td>(55)^b</td></tr> <tr><td>I</td><td>(51)^b</td></tr> </table>	X		F	(68) ^b	Cl	(57) ^b	Br	(55) ^b	I	(51) ^b	248
X													
F	(68) ^b												
Cl	(57) ^b												
Br	(55) ^b												
I	(51) ^b												
	HCl (35%), CH ₂ Cl ₂ , Et ₂ O, rt, 1 h	 (45)	153										
	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (55) ^c	155										
	HCl (35%), CH ₂ Cl ₂ , rt, 1 h	" (81)	153										
	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (52) ^c	155										
	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (14) ^b	155										

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TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

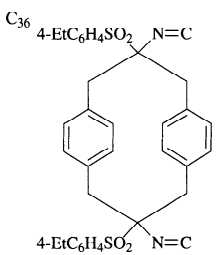
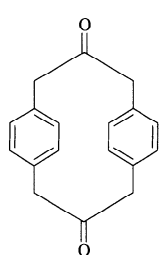
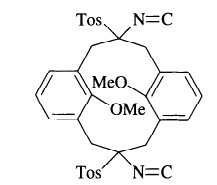
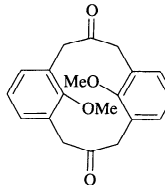
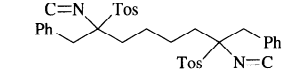
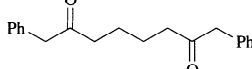
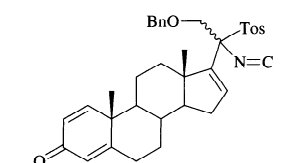
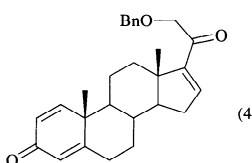
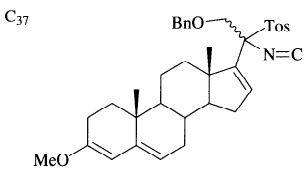
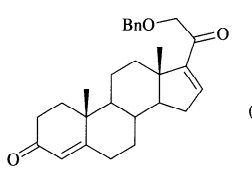
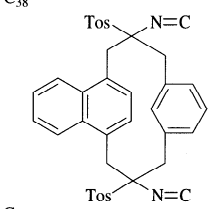
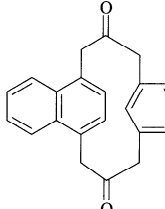
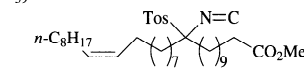
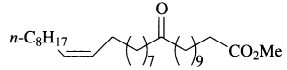
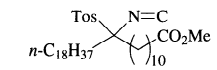
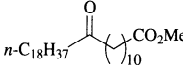
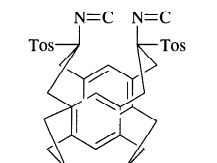
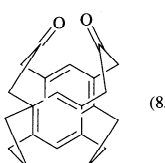
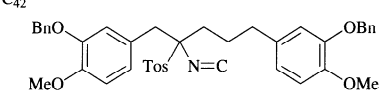
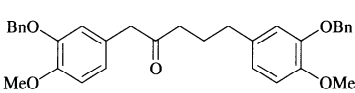
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	HCl (35%), CH ₂ Cl ₂ , rt, 1 h	 (83)	153
	HCl (37%), CH ₂ Cl ₂ , rt, 30 min	(17) ^f	92
	HCl (37%), CH ₂ Cl ₂ , rt, 30 min	(10) ^g	92
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 1 h	 (90)	100
	HCl (37%), CH ₂ Cl ₂ , rt, 1 h	 (57) ^c	110
	HCl (37%), CH ₂ Cl ₂ , rt, 30 min	(57) ^h	92
	HCl (37%), CH ₂ Cl ₂ , rt, 30 min	(29) ^h	92
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 15 min	 (91)	100

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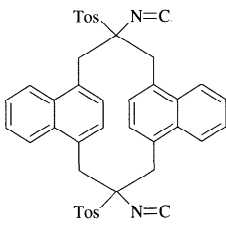
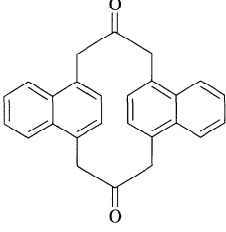
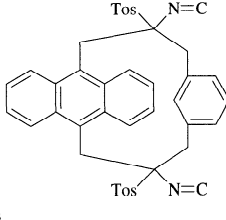
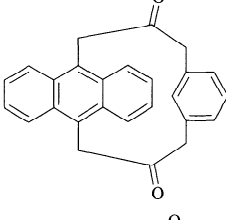
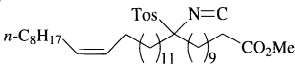
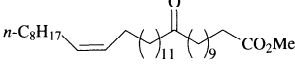
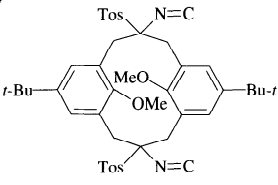
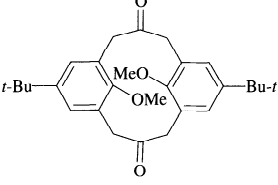
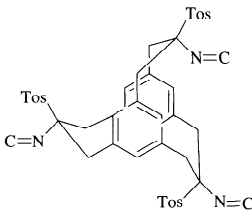
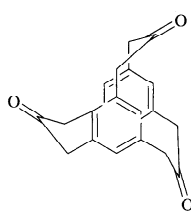
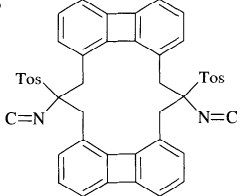
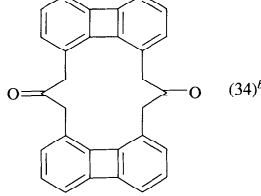
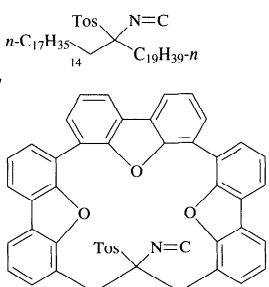
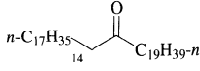
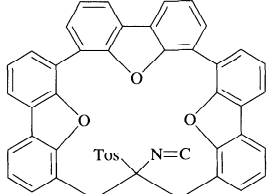
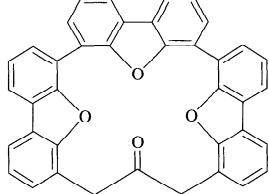
TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₆ 	HCl (37%), CH ₂ Cl ₂ , rt, 1 h	 (28) ^b	249
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 15 min	 (11) ^b	109
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 15 min	 (93)	100
	HCl (37%), CH ₂ Cl ₂ , rt, 2 h	" (19) ^b	110
	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 1.5 min	 (47)	101
C ₃₇ 	HCl (8 N), CH ₂ Cl ₂ , Et ₂ O, 0°, 30 min	 (50)	101
C ₃₈ 	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (44) ^c	155
C ₃₉ 	HCl (37%), Et ₂ O, rt, 2 h	 (—)	252
	HCl (37%), Et ₂ O, rt, 2 h	 (70) ^f	242
C ₄₀ 	AcOH, THF, reflux, 20 h	 (85) ^c	96, 254
C ₄₂ 	Hg(NO ₃) ₂ , THF, rt, 7 h ⁱ	 (68) ^c	96

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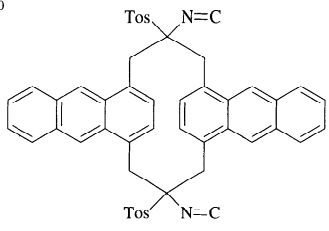
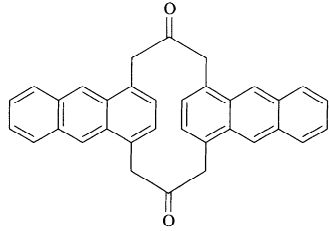
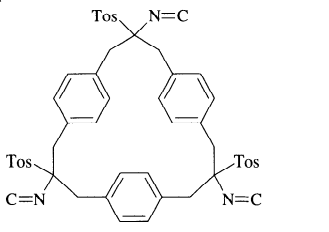
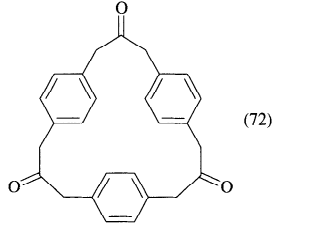
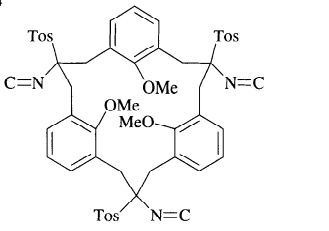
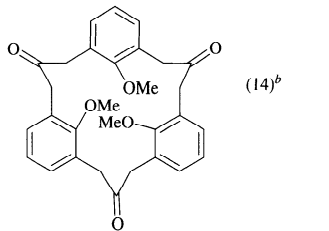
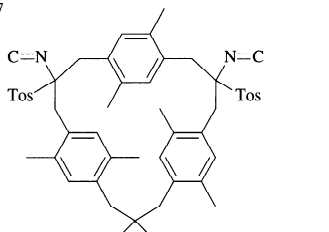
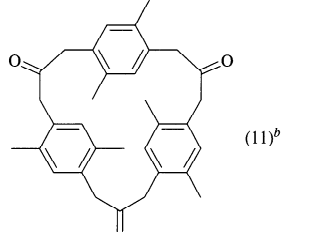
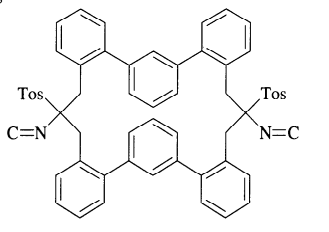
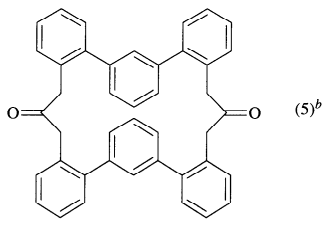
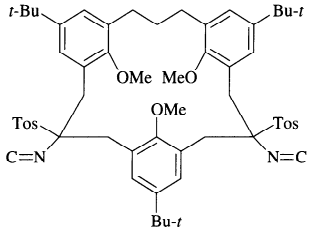
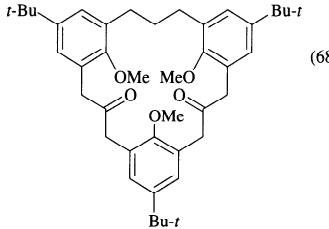
TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (14) ^b	155
	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (39) ^c	155
C ₄₃ 	HCl (37%), CH ₂ Cl ₂ , rt, 2 h	 (94)	160
C ₄₄ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 15 min	 (10) ^b	156
C ₄₅ 	HCl (37%), CH ₂ Cl ₂ , rt, 2 h	 (25) ^b	108, 154
C ₄₆ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 5 min	 (34) ^b	251
C ₄₇ 	HCl (37%), CH ₂ Cl ₂ , rt, 2 h	 (85)	243
	HCl (2 N), C ₆ H ₆ , rt, 6 h	 (7) ^b	150

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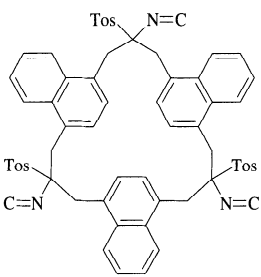
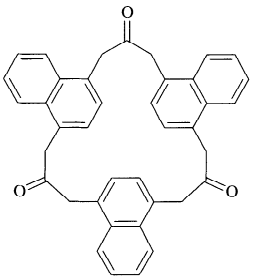
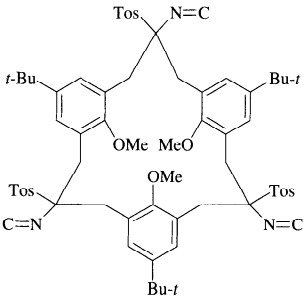
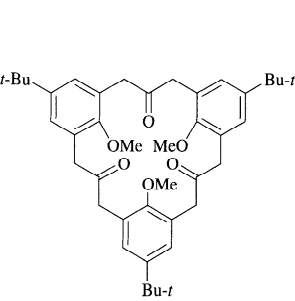
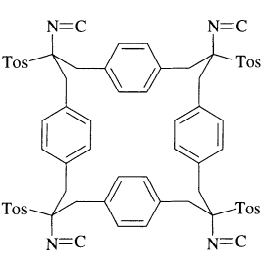
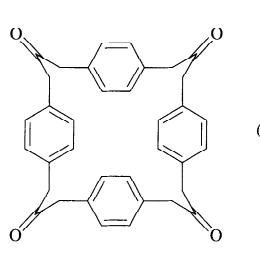
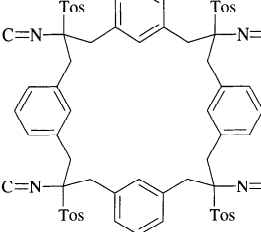
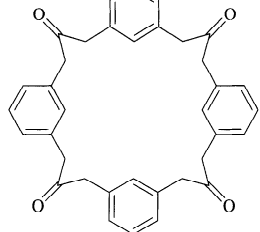
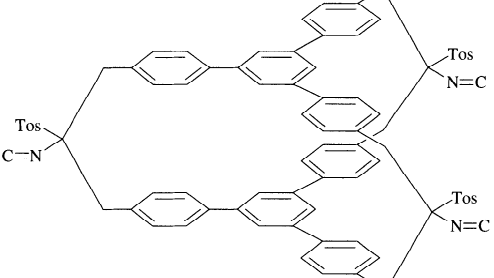
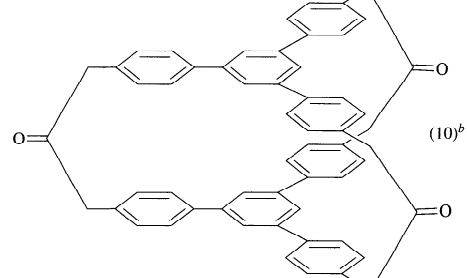
TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅₀ 	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (7) ^b	155
C ₅₁ 	HCl (35%), CH ₂ Cl ₂ , rt, 1 h	 (72)	153, 155
C ₅₄ 	HCl (37%), CH ₂ Cl ₂ , Et ₂ O, rt, 15 min	 (14) ^b	109
C ₅₇ 	HCl	 (11) ^b	250
C ₅₈ 	HCl (37%), CH ₂ Cl ₂ , rt, 10 min	 (5) ^b	253
	HCl (37%), CH ₂ Cl ₂ , DMF, rt, 15 min	 (68) ^b	156

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TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₆₃</p> 	<p>HCl (37%), CH₂Cl₂, rt, 10 min</p>	 <p>(7)^b</p>	155
<p>C₆₆</p> 	<p>HCl (37%), CH₂Cl₂, DMF, rt, 15 min</p>	 <p>(10)^b</p>	156
<p>C₆₈</p> 	<p>HCl (35%), CH₂Cl₂, rt, 10 min</p>	 <p>(13)^b</p>	153, 155
	<p>HCl (35%), CH₂Cl₂, rt, 1 h</p>	 <p>(3)^b</p>	153
<p>C₈₁</p> 	<p>HCl (37%), CH₂Cl₂, rt, 15 min</p>	 <p>(10)^b</p>	154

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TABLE XII. KETONES BY ACID HYDROLYSIS OF DISUBSTITUTED TOSMIC DERIVATIVES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>a</i> Acid hydrolysis does not lead to a cyclopropanone.			
<i>b</i> The yield was based on TosMIC.			
<i>c</i> The yield was based on the monosubstituted TosMIC.			
<i>d</i> The enamide was formed instead of a ketone.			
<i>e</i> The ketone was converted to an acetal in situ.			
<i>f</i> The yield was based on the substituted TosMIC.			
<i>g</i> The yield was based on the isocyanide.			
<i>h</i> The yield was based on the monosubstituted isocyanide.			
<i>i</i> This product was obtained after chromatography over alumina, which effected hydrolysis via the isocyanate.			

TABLE XIII. 1,2-DIKETONES FROM ACID CHLORIDES

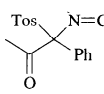
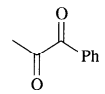
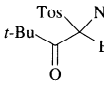
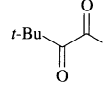
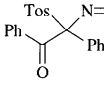
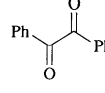
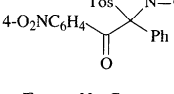
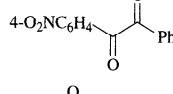
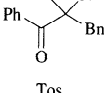
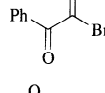

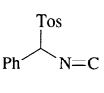
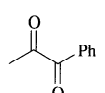
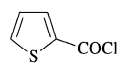
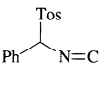
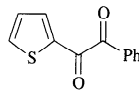
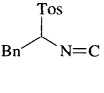
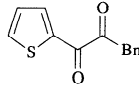
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
(—)		HCl (38%), THF, rt, 2.5 h	 (87)	112
(—)		HCl (38%), EtOH, heat, 5 min	 (73)	112
(—)		HCl (38%), THF, rt, 2.5 h	 (89)	112
(—)		HCl (38%), THF, rt, 2.5 h	 (63)	112
(—)		HCl (38%), THF, rt, 2.5 h	 (50)	112
C ₂ 		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (73)	112
C ₅ 		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (71)	112
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (67)	112, 100

TABLE XIII. 1,2-DIKETONES FROM ACID CHLORIDES (Continued)


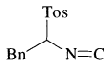
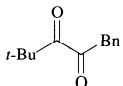
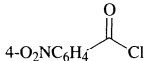
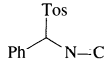
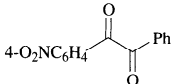
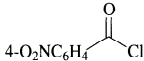
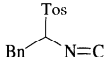
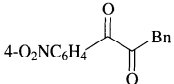

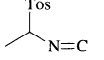


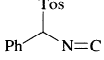
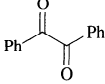

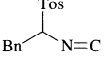
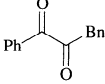

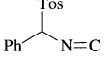
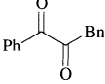
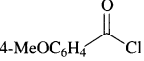
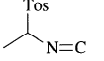
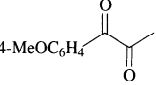
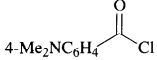
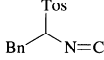
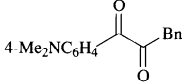
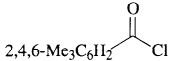
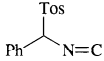
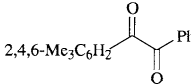

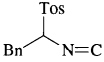
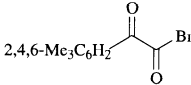
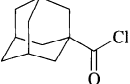
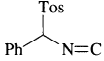
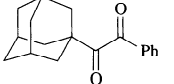

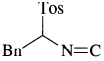
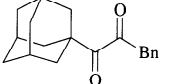
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (52)	112
C ₇ 		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (51)	112
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (65)	112
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (56)	112
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (68)	112
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (51)	112
C ₈ 		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (54)	112
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (57)	112
C ₉ 		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (53)	112, 100
C ₁₀ 		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (29)	112
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (22)	112
C ₁₁ 		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (75)	112, 100
		1. <i>n</i> -BuLi, THF, -80° to rt 2. HCl (38%), THF, rt, 2.5 h	 (22)	112, 100

TABLE XIV. α -HYDROXY KETONES AND α -HYDROXY ALDEHYDES BY HYDROLYSIS OF OXAZOLINES

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁ CH ₂ O		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. HCO ₂ H (60%), rt, 45 min	 (69)	70
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. H ₂ SO ₄ (4 N), rt, 17 h	 I (92)	158
		1. KOH, THF, rt, 3 min 2. H ₂ SO ₄ (4 N), rt, 17 h	 (60) + I (30)	70
		1. MeOH (5 eq), KOH, THF, rt, 1 h 2. HCO ₂ H (60%), rt, 45 min	 (75)	70
		1. MeOH (5 eq), KOH, THF, rt, 1 h 2. H ₂ SO ₄ (2 N), rt, 22 h	 (43)	70
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. HCO ₂ H (60%), rt, 45 min	 (57)	70
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. H ₂ SO ₄ (4 N), rt, 17 h	 (93)	158
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. H ₂ SO ₄ (4 N), rt, 17 h	 (68)	158
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. H ₂ SO ₄ (4 N), rt, 17 h	 (71)	158


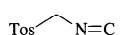
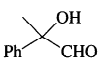
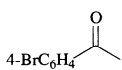
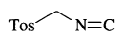
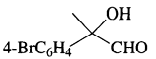
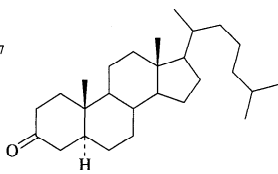
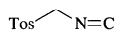
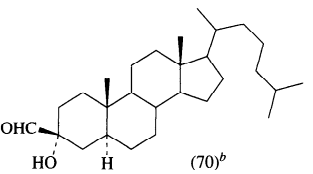
TABLE XIV α -HYDROXY KETONES AND α -HYDROXY ALDEHYDES BY HYDROLYSIS OF OXAZOLINES (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. H ₂ SO ₄ (4 N), rt, 17 h	(73)	158
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. H ₂ SO ₄ (4 N), rt, 17 h	(73)	158
		1. MeOH (10 eq), NaOH (50%), BTEAC, PhMe, rt, 1 h 2. H ₂ SO ₄ (4 N), rt, 17 h	(92)	158
		1. MeOH, Triton B, NaOH (50%), C ₆ H ₆ , rt, 25 min 2. H ₂ SO ₄ (4 N), rt, 24 h	(58)	236
C ₂ CH ₃ CHO		1. K ₂ CO ₃ , MeOH, 30°, 5 min 2. HCl (conc), rt, 10 min	(65)	73
C ₃ C ₂ H ₅ CHO		1. K ₂ CO ₃ , MeOH, 30°, 5 min 2. HCl (conc), rt, 10 min	(52)	73
C ₆ 		1. TIOEt, DME, EtOH, rt ^a 2. HCl (dil.), THF, rt, 17 h	(38) ^b	72
		1. TIOEt, DME, EtOH, rt ^a 2. HCl (dil.), THF, rt, 17 h	(70) ^b	72
C ₇ 		1. TIOEt, DME, EtOH, rt ^a 2. HCl (dil.), THF, rt, 17 h	(78) ^b	72
		1. TIOEt, DME, EtOH, rt ^a 2. HCl (dil.), THF, rt, 17 h	(52) ^b	72
RC ₆ H ₄ CHO		1. K ₂ CO ₃ , MeOH, 30°, 5 min 2. HCl (conc), rt, 10 min	(68)	73
R			(68)	
H			(67)	
4-Cl			(48)	
4-OMe			(60)	
4-Pr-i			(52)	
3-Me				

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TABLE XIV. α -HYDROXY KETONES AND α -HYDROXY ALDEHYDES BY HYDROLYSIS OF OXAZOLINES (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 		1. K ₂ CO ₃ , MeOH, 30°, 5 min 2. HCl (conc), rt, 10 min	 (70) ^b	72
		1. K ₂ CO ₃ , MeOH, 30°, 5 min 2. HCl (conc), rt, 10 min	 (71) ^b	72
C ₂₇ 		1. TIOEt, DME, EtOH, rt 2. HCl (dil.), THF, rt, 17 h	 (70) ^b	72

^a The 4-ethoxyoxazoline was purified.^b The product was a mixture of monomer and dimer.

TABLE XV. ALKANES, *N*-METHYLAMINES, AND ISOCYANIDES BY REDUCTION OF TOSMIC DERIVATIVES

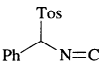
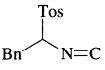
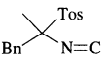
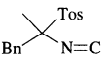
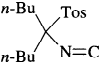
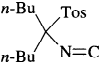
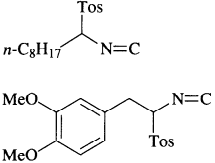
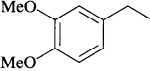
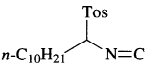
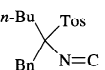
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	LAH, THF, 40°, 30 min	Ph-NHMe (48)	73
C ₁₆ 	Electroreduction	Bn-N=C (46)	161
C ₁₇ 	LAH, THF, 0° to reflux	Bn-NHMe (72)	73
C ₁₇ 	Electroreduction	Bn-N=C (51)	161
C ₁₇ 	LAH, THF, 0° to reflux	<i>n</i> -Bu-NHMe (72)	73
C ₁₇ 	LAH, THF, 40°, 30 min	<i>n</i> -C ₈ H ₁₇ -NHMe (69)	73
C ₁₈ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	 (90)	105
C ₁₉ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	<i>n</i> -C ₁₁ H ₂₄ (92)	105
C ₂₀ 	LAH, THF, 0° to reflux	<i>n</i> -Bu-NHMe (58)	73

TABLE XV. ALKANES, *N*-METHYLAMINES, AND ISOCYANIDES BY REDUCTION OF TOSMIC DERIVATIVES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₂ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	(92)	105
C ₂₃ 	Electroreduction	(75)	161
	Electroreduction	(80)	161
	Electroreduction	(83)	161
	LAH, THF, 0° to reflux	(81)	73
	Li, NH ₃ (liq), EtOH, -33°, 1.5 h	(70)	105
C ₂₄ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	(95)	105
C ₂₅ 	Electroreduction	(74)	161
	Li, NH ₃ (liq), EtOH, -33°, 2 h	(93)	105
C ₂₆ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	(45)	105
	Li, NH ₃ (liq), EtOH, -33°, 2 h	(90)	105
	Li, NH ₃ (liq), EtOH, -33°, 2 h	(91)	105
C ₂₉ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	(90)	105
C ₃₀ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	(90)	105
C ₃₁ 	Li, NH ₃ (liq), EtOH, -33°, 2 h	(95)	105
	Li, NH ₃ (liq), EtOH, -33°, 2 h	(90)	105
	Li, NH ₃ (liq), EtOH, -33°, 2 h	(72)	107
C ₃₆ 	1. Li, NH ₃ (liq), THF, -33°, 2 h 2. HCl, MeOH, reflux, 3 h	(19)	160

TABLE XVI. β -HYDROXY *N*-METHYLAMINES BY REDUCTION OF 4-TOSYLOXAZOLINES

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ CH ₃ CHO		1. CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (-)-(R)- (67)	75
C ₃ 		1. K ₂ CO ₃ , MeOH, rt, 10 min 2. LAH, THF, 0° 3. 35°, 30 min	 (54)	73
C ₄ <i>i</i> -PrCHO		1. K ₂ CO ₃ , MeOH, rt, 10 min 2. LAH, THF, 0° 3. 35°, 30 min	 (58)	73
		1. CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (-)-(R)- <i>i</i> -Pr (67)	75
		1. K ₂ CO ₃ , MeOH, 40°, 25 min 2. LAH, THF, 0° 3. 35°, 30 min	 (55)	73

TABLE XVI. β -HYDROXY *N*-METHYLAMINES BY REDUCTION OF 4-TOSYLOXAZOLINES (Continued)

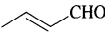
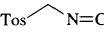
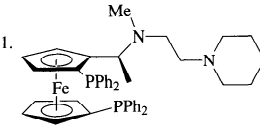
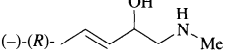
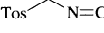
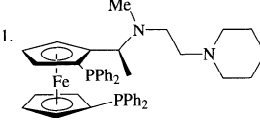
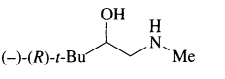

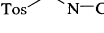
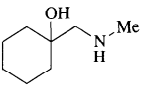
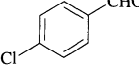
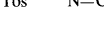
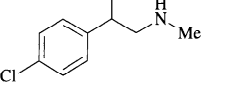
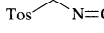
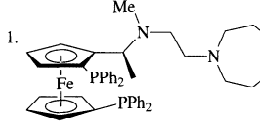
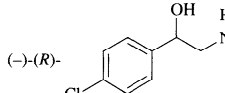
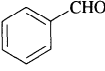

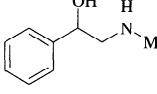
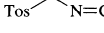
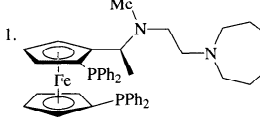
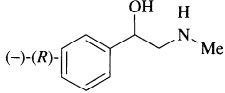
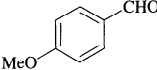

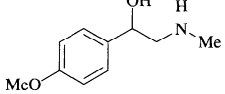

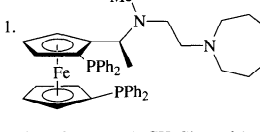
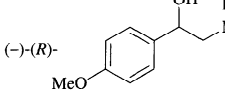
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
		1.  CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (63)	75
C ₅ <i>t</i> -BuCHO		1.  CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (68)	75
C ₆ 		1. K ₂ CO ₃ , MeOH, 40°, 25 min 2. LAH, THF, 0° 3. 35°, 30 min	 (52)	73
C ₇ 		1. K ₂ CO ₃ , MeOH, rt, 10 min 2. LAH, THF, 0° 3. 35°, 30 min	 (66)	73
		1.  CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (84)	75
		1. K ₂ CO ₃ , MeOH, rt, 10 min 2. LAH, THF, 0° 3. 35°, 30 min	 (67)	73
		1.  CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (86)	75
C ₈ 		1. K ₂ CO ₃ , MeOH, rt, 10 min 2. LAH, THF, 0° 3. 35°, 30 min	 (65)	73
		1.  CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (78)	75

TABLE XVI. β -HYDROXY *N*-METHYLAMINES BY REDUCTION OF 4-TOSYLOXAZOLINES (*Continued*)

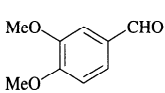
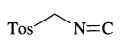
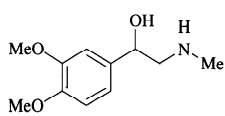
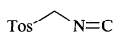
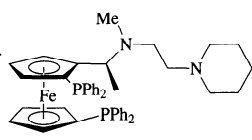
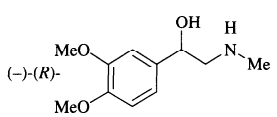
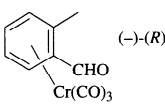
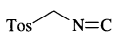
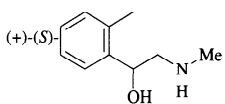
Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 		1. K ₂ CO ₃ , MeOH, rt, 10 min 2. LAH, THF, 0° 3. 35°, 30 min	 (71)	73
		1.  CF ₃ SO ₃ Ag (cat.), CH ₂ Cl ₂ , rt, 2 h 2. LAH, rt	 (83)	75
C ₁₁  (-)-(R)		1. K ₂ CO ₃ , MeOH, 0°, 30 min 2. CH ₂ Cl ₂ , daylight, 3 d 3. LAH, THF, rt, 3 h	 (57)	74

TABLE XVII. α -ADDITIONS TO THE ISOCYANO CARBON OF TOSMIC

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀ Cl ₂		CH ₂ Cl ₂ , -5°	(68)	47, 51
C ₁ MeSCl		(—)	(—)	162
C ₄ (CF ₃ CO) ₂ O		1. CH ₂ Cl ₂ , rt, 10 h 2. H ₂ O	(100)	165
C ₅ <i>t</i> -BuCOCl		60°, 48 h	(100)	163
		—	(100)	163
		C ₆ H ₆ , reflux, 18 h	(67)	164
C ₆ 		—	(—)	162
		—	(—)	162
C ₈ 		C ₆ H ₆ , reflux, 18 h	(70)	164

TABLE XVII. α -ADDITIONS TO THE ISOCYANO CARBON OF TOSMIC (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																												
<p>C₁₀₋₁₈</p> <p>+ H₂N-CH(R¹)-CO₂Me (S) + <i>i</i>-PrCHO</p> <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td></tr> <tr><td>H</td><td>Me</td></tr> <tr><td>Me</td><td>H</td></tr> <tr><td>Me</td><td>Me</td></tr> <tr><td>H</td><td><i>Pr-i</i></td></tr> <tr><td><i>Pr-i</i></td><td>H</td></tr> <tr><td>H</td><td><i>Bu-i</i></td></tr> <tr><td>H</td><td><i>Bu-t</i></td></tr> <tr><td>Me</td><td><i>Pr-i</i></td></tr> <tr><td><i>Pr-i</i></td><td>Me</td></tr> <tr><td>H</td><td>CH₂<i>Bu-t</i></td></tr> <tr><td>Me</td><td><i>Bu-i</i></td></tr> <tr><td>Me</td><td><i>Bu-i</i></td></tr> <tr><td><i>Bu-t</i></td><td>Me</td></tr> <tr><td>H</td><td>Ph</td></tr> <tr><td>Me</td><td>CH₂<i>Bu-t</i></td></tr> <tr><td><i>Pr-i</i></td><td><i>Pr-i</i></td></tr> <tr><td>H</td><td>Bn</td></tr> </tbody> </table>	R ¹	R ²	H	H	H	Me	Me	H	Me	Me	H	<i>Pr-i</i>	<i>Pr-i</i>	H	H	<i>Bu-i</i>	H	<i>Bu-t</i>	Me	<i>Pr-i</i>	<i>Pr-i</i>	Me	H	CH ₂ <i>Bu-t</i>	Me	<i>Bu-i</i>	Me	<i>Bu-i</i>	<i>Bu-t</i>	Me	H	Ph	Me	CH ₂ <i>Bu-t</i>	<i>Pr-i</i>	<i>Pr-i</i>	H	Bn	Tos-N=C	1. MeOH, 0°, 1 h 2. rt, 7 d	 <table border="1"> <thead> <tr> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td>(84)</td><td>—</td></tr> <tr><td>(72)</td><td>58:42</td></tr> <tr><td>(73)</td><td>50:50</td></tr> <tr><td>(80)</td><td>60:40</td></tr> <tr><td>(84)</td><td>81:19</td></tr> <tr><td>(39)</td><td>—</td></tr> <tr><td>(68)</td><td>78:22</td></tr> <tr><td>(59)</td><td>70:30</td></tr> <tr><td>(80)</td><td>81:19</td></tr> <tr><td>(73)</td><td>59:41</td></tr> <tr><td>(65)</td><td>81:19</td></tr> <tr><td>(66)</td><td>79:21</td></tr> <tr><td>(37)</td><td>69:31</td></tr> <tr><td>(75)</td><td>59:41</td></tr> <tr><td>(77)</td><td>54:46</td></tr> <tr><td>(87)</td><td>81:19</td></tr> <tr><td>(76)</td><td>81:19</td></tr> <tr><td>(78)</td><td>77:23</td></tr> </tbody> </table>	I + II	I:II	(84)	—	(72)	58:42	(73)	50:50	(80)	60:40	(84)	81:19	(39)	—	(68)	78:22	(59)	70:30	(80)	81:19	(73)	59:41	(65)	81:19	(66)	79:21	(37)	69:31	(75)	59:41	(77)	54:46	(87)	81:19	(76)	81:19	(78)	77:23	168
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<p>C₁₁</p>	 	CF ₃ CO ₂ H, C ₆ H ₆ , rt, 4 h	(70)	96																																																																												
	 	CF ₃ CO ₂ H, C ₆ H ₆ , rt, 2 h	(88)	96																																																																												
<p>C₁₄</p>	Tos-N=C	1. C ₆ H ₆ , <i>hν</i> , 45°, 1 h 2. 45°, 15 min	(45)	166																																																																												
	Tos-N=C	ZnCl ₂ , Et ₂ O, THF, -40°, 10 d	(10)	167																																																																												

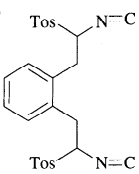
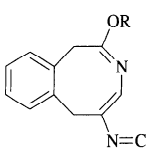
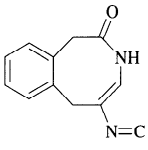
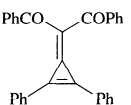
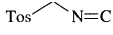
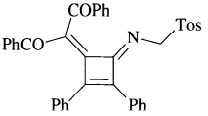
654

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TABLE XVIII. CYCLOADDITIONS TO THE ISOCYANO CARBON OF TosMIC

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ [Cr(CN)(CO) ₅] ⁻ + HBF ₄ + Me ₂ CO		rt, overnight	(53)	292
C ₇ 		C ₆ H ₆ , rt, 1 h	(89)	169
C ₈ 		CHCl ₃ , rt, 5 h	(96)	175
C ₉ 		PhMe, rt, 4 d	(47)	171
C ₁₂ 		1. Cp ₂ Zr(Bu- <i>n</i>) ₂ , THF, -70 to 20° 2. TosMIC, 67°, 15 h 3. MeOH, H ₂ O	(46)	178
C ₁₄ 		1. MeONa, MeOH, rt, 5 min 2. TosMIC, CH ₂ Cl ₂ , 0° 3. AcCl, 0°, ~30 min 4. rt, 1.5 h	(43)	173
C ₁₅ 		Xylene, 100°, 1 h	(74)	170
C ₁₆ 		PhMe, 60°, 1 h	(34)	172
C ₁₇ 		Xylene, 100°, 1 h	(83)	170
C ₁₈ 		CH ₂ Cl ₂ , rt, 24 h	(64)	173
C ₁₉ 		1. THF, ZnCl ₂ , rt, 4 h 2. reflux, 5 h	(84)	177
C ₂₁ 		C ₅ H ₁₂ /CHCl ₃ 4:1, rt, 2 weeks	(49)	293

TABLE XVIII. CYCLOADDITIONS TO THE ISOCYANO CARBON OF TOSMIC (Continued)

Substrate	Isocyanide	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₆ 		KOH, ROH, reflux, 3 h	 R Me (69) Et (74) <i>i</i> -Pr (71)	82a
		<i>t</i> -BuOK, <i>t</i> -BuOH, reflux, 3 h	 (69)	82a
C ₃₀ 		McCN, reflux, 5 h	 (69)	174

14. Acknowledgments

The authors wish to dedicate this Chapter to the workers in the area of TosMIC chemistry. It has been a pleasing challenge—although a time-consuming one—to collect their many contributions and to put these in perspective. Where we have succeeded, this has become possible only through their efforts. As for shortcomings and mistakes of the present survey, the reader has to put the blame on us.

End Throughout this chapter, the tosyl group (4-tolylsulfonyl, *p*-tolylsulfonyl) is abbreviated as Tos, both in names and in formulas, rather than as Ts as is recommended by IUPAC. Not only is the name TosMIC generally accepted, but the Tos abbreviation is also used in nearly all the papers on which this chapter is based.

*

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